

LECTURE NOTES
on
Corrosion Engineering

Compiled by :

Anadi Charan Jena
email: anadicharanjena64@gmail.com
Ph- +91 7008067487



Department of Metallurgical Engineering
Padmashree Krutarth Acharya Institute of Engineering and
Technology, Bargarh, Odisha

Content

Chapter	Page
1.0. Introduction to Corrosion.	4 - 7
1.1. Corrosion	
1.2. Cause of corrosion	
1.3. Corrosion rate expression	
1.4. Cost of corrosion- Direct and indirect losses	
1.5. Importance of corrosion study	
1.6. Classification of corrosion	
1.7. Electrochemical principles of corrosion	
2.0. Electrode Potential and Standard Electrode Potential	8 - 17
2.1. Single electrode potential	
2.2. Electrolysis	
2.3. Electrode reactions	
2.4. Faraday's laws of Electrolysis	
2.5. Applications of Faraday's laws	
2.6. Causes of deviations	
2.7. Electrochemical cells	
2.8. Electrochemical series	
2.9. Applications of EMF series	
2.10. Electrolytic cell	
2.11. Galvanic cell	
2.12. Galvanic series - Importance	
2.13. Concentration cells	
3.0. Different forms of corrosion	18 - 36
3.1. Atmospheric corrosion	
3.2. Intergranular corrosion	
3.3. Pitting corrosion	
3.4. Corrosion fatigue	
3.5. Galvanic corrosion	
3.6. Stress Corrosion Cracking	
3.7. Cavitation corrosion	
3.8. Fretting corrosion	
3.9. High temperature corrosion- Oxidation	
3.10. Stray current corrosion	
3.11. Erosion corrosion	
3.12. Uniform corrosion	
3.13. Underground corrosion	
3.14. Crevice corrosion	

4.0. Control and Prevention of corrosion

37 - 54

4.1. Control of physical, chemical and mechanical characteristics of metals and alloys.

4.1.1. Protective Coatings

4.1.2. Purification of metals

4.1.3. Heat treatment of metals

4.1.4. Alloying

4.1.5. Change in design

4.2. Control of environments - Inhibitor, types , applications

4.3. Control of external source of electric potential

4.3.1. Cathodic protection - advantages and limitations

4.3.2. Anodic protection- advantages and limitations

4.3.3. Passivation

Introduction to Corrosion

1.1. Corrosion :

Destruction or decaying of a material or deterioration in its properties by chemical or or Electrochemical reaction with the environment is called corrosion. It can be fast or slow. For example , sensitized 18-8 stainless steel is badly attacked in hours by polythionic acid while railroad tracks usually show slight rusting. Environments are corrosive to some degrees. Some examples are:

1. moisture and air
 2. fresh, distilled, salt and mine water
 3. rural, urban and industrial atmospheres
 4. steam and other gases such as chlorine, ammonia, hydrogen sulphide, sulphur dioxide and fuel gases
 5. mineral acids such as hydrochloride acid, sulphuric and nitric acid etc.
- Moist air is more corrosive than dry air.
 Hot air is more corrosive than cold air.
 Hot water is more corrosive than cold water.
 Polluted air is more corrosive than clean air.
 Acids are more corrosive than bases or alkalies.
 Stainless steel will outlast ordinary steel.
 No corrosion will occur in vacuum even at high temperatures.
 In general inorganic materials are more corrosive than the organics. For example, corrosion in the petroleum industries is due more to sodium chloride than to oil, naphtha etc. The interaction of metals with the environment could take place at any temperature.

1.2. Cause of corrosion:

Most metals exist in nature in combined forms as oxides, hydroxides, carbonates, chlorides, sulphides etc. As soon as we the metals are extracted from these forms the reverse process begins, i.e nature tries to convert them back into the form they occur. That means metals are chemically unstable in the refined state. The metals have a tendency to revert back to combined state. The process by which the metals have a tendency to go back to the combined state is known as corrosion or weeping of metals

1.3. Rate of corrosion:

Corrosion rate can be expressed as follows:

$$(i) \text{ Mils per year, MPY} = \frac{534 W}{DAT}$$

Where, W = weight loss in milligrams, mg
 D= density of the material, gm/cm³
 A= area of specimen in square inch
 T= exposure time in hours

- (ii) Percentage weight loss
 - (iii) Milligrams per square cm per day
 - (iv) Grams per square inch per hour
- Among these the most accurate method for determining the rate of corrosion is the Mils per year.

1.4. Cost of corrosion- Direct and Indirect losses:

Corrosion losses are two-fold;

- (a) Economic losses
 - (i) Direct losses
 - (ii) Indirect losses
- (b) Conservation of available resources

The total losses by corrosion in industries amount to many billion dollars annually.

The following figure shows some data:

USA- 6 billion dollars

UK. -600 million pounds

Canada- 500 million pounds

Australia- 100 million dollars

India- 154 crore rupees

Japan- 2 lakh dollars

(i) Direct losses:

The direct losses include the cost of replacing corroded structures and machines or their components such as condenser tubes, pipe lines, metal roofing etc. including labour charges, cost of repainting, cost of Cathodic protection, cost of dehumidification of storage rooms etc.

(ii) Indirect losses:

Indirect losses are more difficult to assess and amount to several billion dollars more than the direct losses.

Indirect losses include-

- (a) shut down of the plant
- (b) loss of product (because of leakage)
- (c) loss of efficiency
- (d) contamination of the product(explosions and possible loss of life)
- (e) over design(wastage of material and cost due to over design)

(a) Shut down of the plant: Frequently plants are shut down or portions of a process stopped because of unexpected corrosion failures. For example, the replacement of a corroded tube in an oil refinery may cost a few hundred rupees, but shut down of the unit while repairs are underway, may cost several thousand rupees, in lost production.

(b) Loss of product: Losses of oil, gas, water etc. occur through a corroded pipe system until repairs are made.

(c) Loss of efficiency: This may occur by diminished heat transfer through accumulated corrosion products or by closing the pipes which rust, necessitating increased pumping capacity. In internal combustion engines of automobiles, where piston rings and cylinder walls are continuously corroded by combustion gases and this leads to increased gasoline and oil consumption

(d) Contamination of the product: Contamination of the product by the corrosion product is undesirable and may be harmful in certain cases. Lead equipment otherwise durable is not permitted in storage of food stuffs because of its toxic properties. Similarly soft water flowing through lead piping are not safe for drinking.

(e) **Over design:** In most cases corrosion rates are known, equipment is often designed many times heavier than is required for normal operating conditions. With adequate knowledge of corrosion, more reliable estimates of equipment life can be made and design can be simplified in terms of material and labour.

The losses due to Corrosion varies from country to country depending upon the climatic conditions

1.5. Importance of corrosion study:

Corrosion of metals is a vital concern for the material scientists. This natural phenomenon causes substantial financial losses in various sectors and requires extensive efforts to limit its impact. The objective or importance of corrosion study is to find out the following:

- (a) the reduction of material losses due to corrosion or sudden failure of piping, tanks, metal components of machines, hulls, marine structures etc
- (b) the conservation, which is limited and wastage of which includes corresponding losses of energy and water resources accompanying the production and fabrication of metal structures. Hence to minimize the effects of corrosion, we must carefully observe or study its mechanism.

1.6. Classification of corrosion:

Corrosion has been classified in many ways depending upon the corrosive environment. One method divides corrosion into low temperature corrosion and high temperature corrosion. Another classifies corrosion into

1.6.1. *Dry corrosion*

1.6.2. *Wet corrosion*

1.6.3. *Direct chemical corrosion and*

1.6.4. *Electrochemical corrosion*

1.6.1. Dry corrosion :

In dry corrosion a metal or nonmetal is attacked by a corrosive gas or vapours. It is often associated with high temperatures. exp. Attack on steel by furnace gas.

1.6.2. Wet corrosion :

Wet corrosion occurs when a liquid is present. This usually involves aqueous solutions or electrolytes and accounts for the greatest amount of corrosion by far. A common example is corrosion of steel by water. The presence of even a small amount of moisture could change the corrosion picture completely. For example, dry chlorine is practically non-corrosive to ordinary steel, but moist chlorine or chlorine dissolved in water is extremely corrosive and attacks most of the common metals and alloys. The reverse is true for titanium - dry chlorine is more corrosive than wet chlorine.

1.6.3. Direct chemical corrosion :

Direct chemical corrosion is essentially a chemical attack and occurs as a result of chemical reactions between the materials particularly metals and corrosive solutions such as acids. The attack under these conditions is uniform, relatively high and continues at an almost constant rate. Reactions of dry chlorine, hydrogen sulphide, oxygen, or other gases with dry metals are examples of direct chemical attack. One means of controlling direct chemical corrosion is the addition of certain inhibitors in the corrosive solutions.

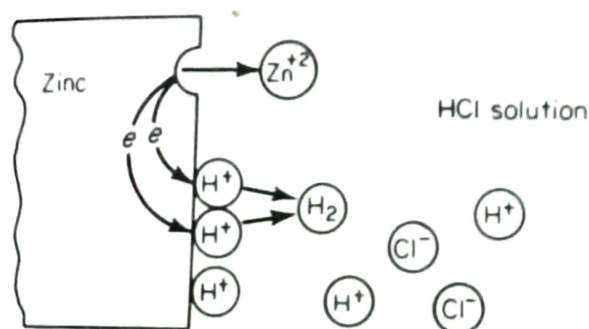
1.6.4. Electrochemical corrosion :

This type of corrosion occurs at or near room temperature as a result of reactions of metals with water or with aqueous solutions of salts, acids or bases and involves a transfer of electrons. In all these cases, there should be a flow of electricity for certain areas of the metal surface to other areas through the solution known as

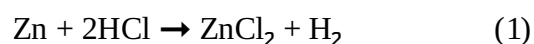
electrolyte, capable of conducting electricity and there must exist a difference of potentials either between two dissimilar metals or between two different areas on the surface of the metal. In all cases, there should be a flow of electrons in certain areas of the metal surface to other areas through the solution known as electrolyte, which is capable of conducting electricity and there must be a difference of potentials either between the two dissimilar metals or between the two different areas of the surface of the metal.

As a result of structural and chemical inhomogeneity existing in metals and environment the metal surface develops anodic and cathodic sites. The term anode is used to describe that portion of the metal surface that is corroded and dissolves as ions and from which current leaves the metal to enter into the solution. Such transfer of ions is known as anodic oxidation. The term cathode is used to describe the metal surface from which current leaves the solution and returns to the metal, hence cathodic reaction is a reduction type and the metal is not affected. The rate of reaction depends on the amount of current between anodic and cathodic sites and the nature of electrolyte. Highly pure single phase metals corrode at a slower rate than impure metals and alloys containing more phases.

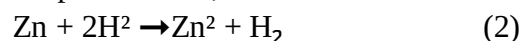
The Electrochemical nature of corrosion can be illustrated by the attack on zinc by hydrochloric acid. When zinc is placed in dilute hydrochloric acid, a vigorous reaction occurs, hydrogen gas is evolved and zinc dissolves forming zinc chloride. It is illustrated in the following figure.



(Fig. 1.1 Electrochemical principle of corrosion of Zn in HCl.)



Noting that the chloride ion is not involved, this equation can be written in the simplified form,

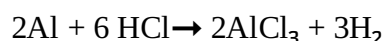
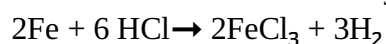


Hence zinc reacts with the hydrogen ions of the acid solution to form zinc ions and hydrogen gas and it can be seen that zinc is oxidised to zinc ions and hydrogen ions are reduced to hydrogen. The equation (2) can be divided into two reactions such as oxidation of zinc and reduction of hydrogen ions;

Oxidation (anodic reaction)- $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

Reduction(cathodic reaction) - $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

An oxidation or anodic reaction is indicated by an increase in valence electrons and a reduction or cathodic reaction by a decrease in valence electrons. Both the reactions occur simultaneously and at the same rate on the metal surface. Similarly like zinc, iron and aluminium are corroded by hydrochloric acid. The reactions are

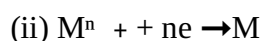


CHAPTER 2

Single Electrode Potential & Standard Electrode Potential

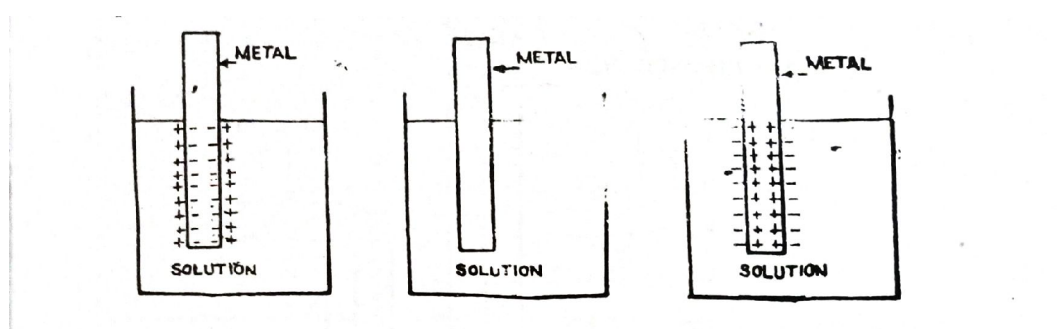
2.1. Single electrode potential

When an electrode is immersed in an electrolyte containing its own ions, two types of reactions occur as shown in fig.2.1 below.



As a result of these reactions electrodes acquire charge. It will acquire -ve charge when metal dissolution reaction occurs at the surface and acquire +ve charge when metal deposition reaction occurs. The dissolution and the deposition reactions will continue till equilibrium is reached between the electrode surface and the electrolyte adjacent to the electrode surface. At the surface of separation between the electrode and solution, a difference of electrical potential exists. This difference in electrical potential is known as single electrode potential or half cell potential. On the other hand, the tendency of an electrode to loss or gain electrons is called electrode potential. It is denoted by the symbol "E".

Standard electrode potential is the potential of a half cell reaction when the reactants and products are of unity activities and the temperature is kept at 298° K. If gas involved the standard conditions chosen 298°K and 1 atm pressure. It is denoted by the symbol "E°"

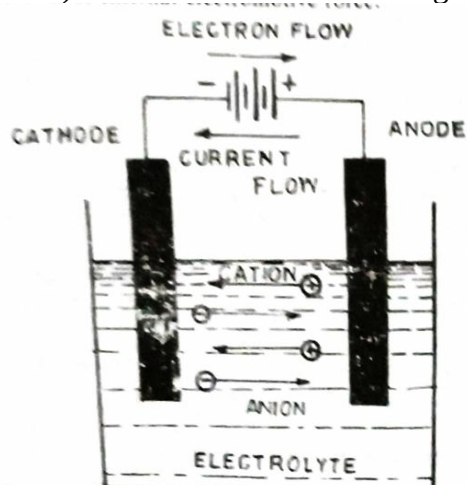


(Fig. 2.1. Metal electrode immersing in electrolyte containing its own ions)

2.2 Electrolysis :

It is the process of decomposition of an electrolyte by the passage of electricity. The apparatus used for electrolysis is called the electrolytic cell in which electrical energy is used to cause a chemical reaction to take place (as shown in fig. 2.2). Electrolysis of an electrolyte can be carried out by dipping two metallic rods or plates in the solution and connecting them by means of a wire to the two terminals of a battery which is a source of EMF (Electro Motive Force). During electrolysis the

passage of current is accompanied by migration of ions. Positively charged ions (cations) are attracted towards the negatively charged electrode (cathode), while



(Fig. 2.2. Process of electrolysis)

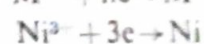
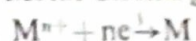
the negatively charged ions (anions) are attracted towards the positively charged electrode (anode).

2.3 Electrode reactions :

(A) Cathode and cathodic reactions :

The electrode which supplies electrons is called the cathode. Cathodes can be made of metals, alloys or graphite in the form of sheets, sticks etc. At cathode reduction reaction occurs. The cathodic reactions are given below:

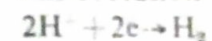
1. Metal discharge



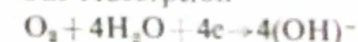
2. Reduction of anion from higher to lower valency



3. Gas evolution



4. Gas Absorption



(B) Anode and anodic reactions :

The electrode which gets electrons is called the anode. Anodes can be of two types:

(i) Soluble anodes : These anodes participate in the Electrochemical processes. Soluble anodes are generally metallic such as copper in copper refining.

(ii) Insoluble anodes : Insoluble anodes do not participate in electrochemical processes. Insoluble anodes are generally made of noble metals such as platinum,

palladium, iridium and to certain extent gold and also carbon or graphite. At anode, oxidation reactions occur. Anodic reactions are given below:

1. Dissolution of a metal
 $M \longrightarrow M^{n+} + ne$
 $Ni \longrightarrow Ni^{3+} + 3e$
 $Cu \longrightarrow Cu^{2+} + 2e$
2. Gas evolution
 $4(OH)^- \longrightarrow 2H_2O + O_2 + 4e$
 $2Cl^- \longrightarrow Cl_2 + 2e$
3. Absorption of a gas
 $H_2 \longrightarrow 2H^+ + 2e$
4. Oxidation of anion from a lower to a higher valency
 $Fe^{2+} \longrightarrow Fe^{3+} + e$

2.4. Faraday's laws of electrolysis :

The relation between the quantity of electricity passed and the amount of substances formed or deposited at the electrodes is formulated by Faraday in the form of two independent laws, which are

(1) *Faraday's First Law:*

This law states that "for the same electrolyte, the amount of substance deposited or liberated or dissolved at an electrode is directly proportional to the quantity of electricity passed through the solution." Thus according to this law

$$W \propto I \times t \quad (I \times t = \text{quantity of electricity})$$

$$\text{or } W = Z \times I \times t$$

Where,

W = weight of substance formed at the electrode by the passage of current of I amperes for t seconds.

Z = Electrochemical equivalent of a substance.

If when, $I = 1$ ampere, $t = 1$ second, then

$$W = Z.$$

So, Electrochemical equivalent of a substance is the mass of substance which is deposited during electrolysis by the passage of a steady current of 1 ampere for second. i.e 1 coulomb of electricity.

(2) *Faraday's Second Law :*

It states that "When same quantity of electricity is passed through different electrolytes, the amount of different substances deposited at the electrodes is directly proportional to their equivalent weights." Mathematically,

$$W \propto E$$

Where,

W = weight of substance deposited by the passage of certain quantity of electricity, E = equivalent weight, which is defined as the atomic weight divided by the Electrochemical valency (n). i.e. $E = A/n$.

Thus, H^+ , Ag^+ , $1/2 Cu^+$, $1/2 Fe^{2+}$, $1/3 Fe^{3+}$ etc. are equivalent to one another. It follows that a given quantity of electricity will deposit twice the amount of metallic copper from a Cu^+ salt than from one containing Cu^{2+} ions.

From this law it follows that the same amount of electricity is required to liberate 1

gm equivalent of substance from any electrolyte. This quantity is called Faraday and denoted by F . From the Faraday's second law, 1 gm equivalent of substance will be deposited by 96,500 coulombs. Thus, A/n gms of substance will be deposited by 96,500 coulombs.

W gms of substance will be deposited by $= (F \times W) / (A/n)$ coulombs.

Quantity of electricity = current \times time

$$(F \times W) / (A/n) = I \times t$$

$$\text{Or, } W = \frac{I \times t \times A}{F \times n} \quad (2.1)$$

This equation represents the combined form of Faraday's first and second law.

2.5. Applications of Faraday's laws of electrolysis :

Faraday's laws are applicable to both aqueous and fused electrolytes. The basic expressions of Faraday's laws of electrolysis may be manipulated to describe a range of metal finishing and related processes. The following are some of the applications.

- Extraction of Metal from their Ores. ...
- Refining of Metals. ...
- Manufacturing of Chemicals. ...
- Electro-Deposition. ...
- Electroplating. ...
- Electro-deposition of Rubber. ...
- Electro-Metallization. ...
- Electro-Facing.

In each case, the applications of Faraday's laws is illustrated by means of worked examples.

2.6. Causes of Deviations :

When Faraday's laws are tested experimentally, the apparent deviations from these laws are observed experimentally with both fused and aqueous electrolytes. Deviations arise due to the following reasons :

(a) Discharge of other ions : Current loss occurs due to the discharge of ions of impurities or even necessary components of electrolyte at electrodes. For example, electrolysis of acidified zinc sulphate doesn't lead to the deposition of one gram equivalent of zinc at cathode for each faraday of current due to discharge of H^+ ions along with Zn^{2+} ions.

(b) The formation of compound at the electrode : In certain cases, the formation of compound at electrode results in current loss. For example, in electrolysis of fused $BiCl_3$, chlorine is liberated at the anode, while no metal is formed at the cathode due to the formation of compound.

(c) The dissolution of the electrode: Current loss can also be occurred due to the dissolution of electrode in the electrolyte mainly in case of fused salt.

(d) Recombination of primary products: The cathodic *products of electrolysis* may combine with anodic gases and form original salt. The reaction forming original salt causes current losses. This is more in case of fused salt electrolyte due to their high temperature

(e) Mechanical losses: There can be mechanical loss of the substances formed at the electrodes depending on the structure of the deposit. This factor can be present with both fused and aqueous electrolytes.

(f) Evaporation losses : This is only present in salts of metals having high vapour pressure e.g. in electrolysis of NaCl. High temperature promotes the evaporation of the metal.

2.7. Electrochemical Cells :

A cell is a single arrangement of two electrodes, usually metallic immersed in an electrolyte and in which chemical reactions generate electricity.

The essential components of an Electrochemical cell are

1. Electrolyte (ionic conductor)
2. Anode
3. Cathode
4. External circuit (electronic conductor)

Each cell is made of two electrodes . In electrochemical cell, cathode is one where reduction reaction occurs while anode is one where oxidation reaction occurs. Electrochemical cells can be reversible or irreversible. Cell is reversible when chemical reactions at the electrodes are the same but reversed in direction when the direction of flow of current is reversed. Cell is irreversible when different reactions occur at one or both electrodes when the direction of current is reversed.

Cell potential or EMF (Electro Motive Force) of a cell :

An electrochemical is made up of two half cells i.e two electrodes. One of these electrodes must have higher electrode potential (higher tendency to loss electrons) than the other electrode. As a result of this potential difference , the elections flow from one electrode at higher potential to an electrode at lower potential. Thus, the difference between the electrode potential or two half cell is known as emf of the cell or cell potential or voltage.

2.8. Electrochemical Series or EMF Series:

When metals are arranged in order of their standard electrode potential,a series is formed which is known as electrochemical series or EMF series. This is a classification of metals in order of their electro positivity i.e their tendency to loose elections

The following table shows such classification.

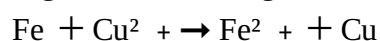
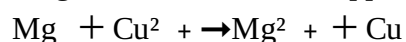
Table 2.1 (EMF series)

Electrode Reaction	E° (volts), 25°C	
Na = Na ⁺ + e	(Base)	+2.712 (Anode)
Mg = Mg ²⁺ + 2e	↑	+2.34
Al = Al ³⁺ + 3e		+1.67
Zn = Zn ²⁺ + 2e		+0.762
Cr = Cr ³⁺ + 3e		+0.71
Fe = Fe ²⁺ + 2e		+0.440
Ni = Ni ²⁺ + 2e		+0.250
Sn = Sn ²⁺ + 2e		+0.136
Pb = Pb ²⁺ + 2e		+0.126
<hr/>		
H ₂ = 2H ⁺ + 2e		0.00
<hr/>		
Cu = Cu ²⁺ + 2e		-0.345
Cu = Cu ⁺ + e		-0.522
Ag = Ag ⁺ + e		-0.800
Pt = Pt ²⁺ + 2e		-1.2
Au = Au ³⁺ + 3e		-1.42
Au = Au ⁺ + e	(Noble)	-1.62 (Cathode)

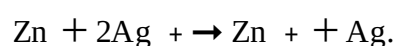
2.9. Applications of EMF Series:

The EMF series is very useful in electrometallurgy as it is very helpful in the interpretation of electrode reactions in electrochemical cells and electrolytic cells. Some of the applications are

1. Displacement of metals : A metal will replace another metal below in series i.e more electropositive metal will displace a less electropositive metal from its salts in aqueous solution. The more electropositive metal is oxidised and less electropositive metal is reduced. For example,
Magnesium and Iron in copper sulphate solution

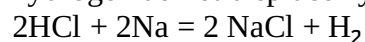


Zinc in Silver Nitrate solution



2. Displacement of Hydrogen :

Metals above in the series displace hydrogen from acids, while metals below hydrogen do not displace hydrogen from acids. For example,



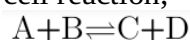
3. Electrolysis: Least electropositive metal deposits first. For example,

From acidified solution containing both H⁺ and Cu²⁺, Copper is liberated first

4. Corrosion and protection: The elements at the upper end of the emf series are very active and their takes place quite readily. All metals above Copper rusts fairly easily in the atmosphere but metals below copper do not rust so easily.

Nernst Equation :

It gives the effect of concentration on electrode potential. Concentration of electrolyte affects electrode potential to a considerable extent. For a generalized reversible half cell reaction,



$$\Delta G = \Delta G^\circ + RT \ln \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b}$$

Here the a's in numerator and denominator are the activities of the products and reactants respectively, ΔG is the free energy of the reaction when the activities of the products and the reactants are unity.

Using the above equations, we ge

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b}$$

2.10. Electrolytic Cell :

It is just the reverse of electrochemical cell. It is a device in which electrical energy is converted into chemical energy and the products are thermodynamically less stable than the reactants. The main components of electrolytic cell are

- (a) Electrolyte
- (b) Anode
- (c) Cathode
- and (d) External power supply

Electrolytic cells are used for electroplating, electrowinning, electroforming, electromachining etc.

Characteristics : The electrolytic cells should have the following requirements:

1. It should consume little energy per unit weight
2. It should have high output.
3. It should be easy to operate.
4. It should provide complete recovery of desired electrolysis products
5. It should be corrosion resistant to the electrolyte.
6. It should be resistant to heat.

Difference - electrochemical cell and electrolytic cell

Type	Electrochemical cell	Electrolytic cell
1. Cathode sign	(+)	(-)
2. Anode sign	(-)	(+)
3. Cathodic reactions	Reduction	Reduction
4. Anodic reaction	Oxidation	Oxidation

2.11. Galvanic Cell :

A galvanic cell is a device which converts chemical energy into electrical energy. The emf arises due to chemical reactions within the cell. Galvanic cells are also called voltaic or chemical cells. Daniel cell is a well known example of galvanic cell.

In galvanic cell, chemical reactions involve release or acceptance of electrons when two dissimilar metals are in contact with electrolyte containing their own ions. The cell can be represented as

Anode | Anodic electrolyte || Cathodic electrolyte | Cathode

Zn | ZnSO₄ || CuSO₄ | Cu (Daniel cell)

Zn | Zn²⁺ + 2e⁻ || Cd²⁺ + 2e⁻ | Cd .

Galvanic cells are of two types:

(i) *Galvanic cells with transference*: These cells are characterized by the presence of a liquid junction potential between two electrolyte solutions of different concentrations and compositions.

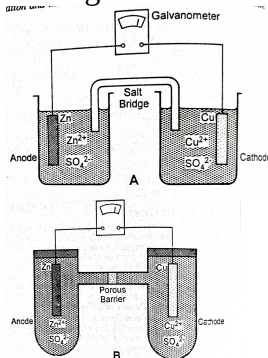
Exp. Zn | Zn²⁺ + 2e⁻ || Cu²⁺ + 2e⁻ | Cu

Zn | Zn²⁺ + 2e⁻ || Cd²⁺ + 2e⁻ | Cd

(ii) *Galvanic cells without transference*: These cells are characterized by the absence of liquid junction potential at phase boundary between two different solutions.

Exp. Pt—H₂ | HCl || Cl₂—Pt.

The figures show the representation of galvanic cell:



The emf of galvanic cell is due to the potential difference between various combinations of metals. It consists of two compartments each of them is called a half cell. The half with more negative potential is called anode and the cathode. At anode, an oxidation reaction occurs while on cathode a reduction reaction occurs.

The emf of galvanic cell without transference is given by the sum of the emfs of two half cell reactions.

Thus,

$$E_{\text{cell}} = E_1 + E_2$$

Similarly emf of galvanic cell with transference is given by

$$E_{\text{cell}} = E_1 + E_2 + E_j$$

where, E_j = liquid junction potential

The values of E_1 and E_2 are calculated by

Nernst equation.

2.12. Galvanic Series - Importance :

Since galvanic cells are formed due to two dissimilar metals in contact, in the presence of an electrolyte, one metal becomes anodic and therefore corroded. By taking pairs of metals and alloys in an given medium such as sea water and observing which becomes the anode, a series can be prepared, known as galvanic series. The galvanic series of many metals and alloys is given in the following table.

TABLE- Galvanic Series

Noble or Cathodic ↑ INCREASING REACTION ↓ Active or Anodic	Platinum
	Gold
	Graphite
	Titanium
	Silver
	[Chlorimet 3 (62 Ni, 18 Cr, 18 Mo)
	[Haste alloy C (62 Ni, 17 Cr, 15 Mo)
	[18-8 Mo Stainless Steel (Passive)
	[18-8 Stainless Steel (Passive)
	[Chromium Stainless Steel (11–30% Cr (Passive)
	[Inconel (80 Ni, 13 Cr, 7Fe) (passive)
	[Nickel (Passive)
	Silver solder
	[Monel (70 Ni, 80 Cu)
	[Cupronickels (60–90 Cu, 40–10 Ni)
	Bronzes (Cu–Sn)
	Copper
	[Brasses (Cu–Zn)
	[Chlorimet 2 (66 Ni, 32 Mo, 1 Fe)
	[Hastealloy B (60 Ni, 30 Mo, 6Fe, 1 Mn.)
	[Inconel (active)
	[Nickel (active)
	Tin
	Lead
	Lead tin solders
	[18–8 Mo Stainless Steel (active)
	[18–8 Stainless Steel (active)
	Ni–Resist (high Ni Cast iron
	Chromium Stainless Steel. 13% Cr (active)
	[Cast Iron
	[Steel or Iron
	2024 Aluminium (4.5 Cu, 1.5 Mg, 0.6 Mn)
	Cadmium
	Commercially pure Aluminium
	Zinc
	Magnesium and Magnesium Alloy

Applications/ importance of galvanic series : Some of the applications include

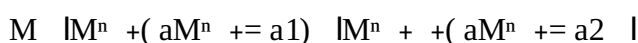
1. The metals and alloys at the top of the series are corroded least while in the bottom are corroded to the maximum extent.
2. The farther the metals and alloys in the series, the greater the potential generated. Therefore metals and alloys which are farther apart in the series should not be coupled together.
3. When metals and alloys of the same group (shown brackets) are coupled together, there is a little danger of corrosion.
4. Same metal can assume different position in the series.

2.13. Concentration Cells :

The cell where emf arises by transfer of material from one electrode to the other due to concentration gradient is called the concentration cell. The concentration gradient may be due to any of the following situations:

(a) The change in concentration in electrolyte.

exp.



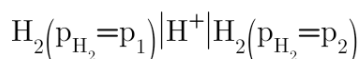
(b) The change in concentration of electrodes.

Exp. The amalgam or alloy electrode having heterogenous composition,



exp.

Gas electrode at different pressure of gases

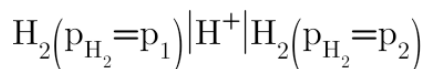


The electrode in dilute solution acts as an anode while the electrode in concentrated solution acts as a cathode.

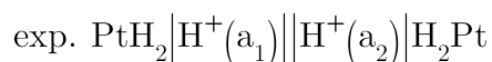
Concentration cells are of two types:

1. Concentration cell without transference -- These type of cells are characterized by the absence of liquid junction potential

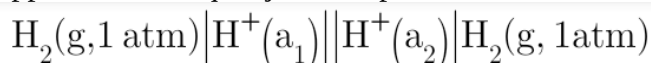
Exp.



The liquid junction potential can be eliminated by a salt bridge.



2. Concentration cell with transference:- These cells are characterized by the appearance of liquid junction potential between the two solutions. for example



Different Forms of Corrosion

There are different types of corrosion and their mechanisms and preventing measures are described in detail below:

3.1. Atmospheric Corrosion :

The heaviest toll of corrosion is due to the corrosion in natural environments. It is the most common type of corrosion and causes serious damage unless adequate measures are adopted. It is mainly due to the combined effects of film formation and film breakdown. The formation of protective film occurs due to the oxidizing action of air on a metal surface and the film breakdown is the result of electrochemical action. The presence of moisture on the metal surface is necessary for Film breakdown.

Some examples of atmospheric corrosion are examples are:

1. Rusting of iron
2. Surface deterioration of Zinc and Al alloys
3. Formation of patina on copper.

Factors affecting atmospheric corrosion :

The most important factors affecting this type of corrosion are as follows:

(a) Degree of humidity : The rate of atmospheric corrosion depends upon the moisture content in the atmosphere. For metals, there is a critical humidity above which the rate of corrosion increases sharply. For example, rusting of iron is very low below 60% relative humidity while it occurs severely if the humidity is above 80 %..

(b) Contents of the atmosphere : The atmospheric corrosion is mainly due to moisture and oxygen, but it is increased by the presence of contaminants in the atmosphere such as:

1. Presence of hygroscopic salt- Certain hygroscopic salts such as ammonium sulphate or sodium chloride, if present, settle on the metal surface and accelerate the corrosion rate.
2. Presence of SO₂ - It is the main contaminant of the atmosphere. It reacts with moisture to form sulphuric acid and sulphurous acid which are both corrosive and increase the rate of corrosion.
3. Presence of chlorides - In many cases corrosion in form of pits can be seen on the surface of aluminium and chromium due to the presence of chlorides in the atmosphere.

Prevention of Atmosphere Corrosion :

Atmospheric corrosion can be minimised or prevented by the following measures:

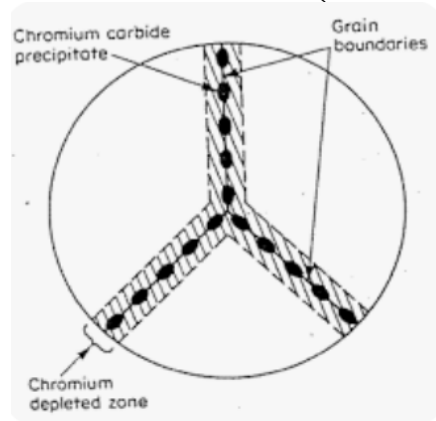
1. Applying coatings

2. Addition of inhibitors
3. Cathodic protection method.

3.2. Intergranular Corrosion :

Localized attack at and adjacent to grain boundaries with relatively little corrosion of the grains is the intergranular corrosion. The alloy disintegrates grains and loses its strength. Intergranular corrosion can be caused by impurities at the grain boundaries, enrichment of one of the alloying elements or depletion of one of these elements in the grain boundary areas.

For example, depletion of chromium in the grain boundary regions results in intergranular corrosion of stainless steel (shown in fig.3.1)



(Fig.3.1. Intergranular corrosion of 18-8 stainless steel)

The almost universally accepted theory of intergranular corrosion is based on the impoverishment or depletion of chromium in the grain boundary areas. The chromium depleted regions become anodic with respect to other regions containing more chromium and hence get corroded. Generally addition of chromium to ordinary steel impacts corrosion resistance to the steel in many environments. At least 10% chromium is needed to make a stainless steel. If the chromium content is effectively lowered, relatively poor corrosion resistance of ordinary steel is approached. In the temperature range 950°-1450°F, the chromium carbide is virtually insoluble and precipitates out of solid solution if carbon content is about 0.03% or higher. The chromium is thereby removed from solid solution and the result is the metal with lowered chromium content in the area adjacent to grain boundaries. The chromium carbide in the grain boundary is not attacked. The chromium depleted zone near the grain boundary is corroded because it doesn't contain sufficient corrosion resistance to resist attack in many corrosive environments. The carbon diffuses towards the grain boundary quite readily.

On the other hand, the grain boundaries contain material which shows electrode potential more anodic than that of a grain centre in a particular corroding medium. As a result certain compounds are precipitated at the grain boundaries and leave the solid solution, just adjacent to the grain boundary, impoverished in one constituent. This impoverished solid solution acts as anodic areas with respect to the grain centre and to the precipitated compounds and hence attacked by the corrosive environment.

Prevention of intergranular corrosion : Intergranular corrosion can be prevented or minimized by;

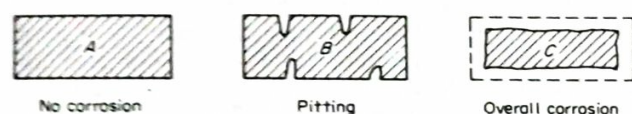
1. Employing high temperature solution heat treatment - It is also known as quench - annealing or solution quenching. It consists of heating to 1950 to 2050 °F followed by water quenching. Chromium carbide is dissolved at these temperatures and a more homogeneous alloy is obtained. If cooling is very low, the entire structure will be susceptible to intergranular corrosion.
2. Adding elements that are strong carbide formers, called stabilizers. - The strong carbide formers, columbium or columbium plus tantalum and titanium are added in sufficient quantity to combine with all of the carbon in the steel.
3. Lowering the carbon content to below 0.03 % . - Lowering the carbon to below 0.03% does not permit sufficient carbide to form to cause intergranular corrosion attack in most applications.

3.3. Pitting Corrosion

Pitting corrosion is a localised attack on the metal surface, resulting in the formation of pits, holes or cavities and these may penetrate deep into the metal surface causing destruction of pipes and tubes of various types. Pits are sometimes isolated or so close together that they look like a rough surface. This is one of the most troublesome form of corrosion.

Characteristics of pitting corrosion :

1. The attack is confined to very small areas of the metal surface, the bulk of which remain unattacked.
2. Pits usually grow in the direction of gravity. Most pits develop and grow downward from horizontal surfaces.
3. Once started, a pit penetrates the metal at an ever increasing rate.
4. Pits tend to undermine or undercut the surface as they grow.
5. Active metals are most susceptible to this form of corrosion. e.g. Cr and Al and their alloys, stainless steel.
6. It may be considered as the intermediate stage between general overall corrosion and complete corrosion resistance as shown in the following figure.



(Fig. 3.2 pitting corrosion)

Factors affecting pitting corrosion

1. Stainless steels are more susceptible to damage by pitting corrosion than are any other group of metals and alloys.
2. Severe cold working increases the pitting attack.
3. Pitting and localised corrosion are less likely to occur on polished than on etched or ground surfaces. The pits formed on polished surfaces are larger and penetrate more rapidly than those on rough surfaces.
4. The agents which are most active in causing pitting corrosion are chloride, bromide and hypochloride ions.

5. Pitting is usually associated with stagnant conditions such as a liquid in a tank. Velocity or increasing velocity often decreases pitting attack. For example, a stainless steel pump would give good service if it were run continuously in sea water, but would pit if it were shutdown for extended periods.

Prevention of pitting corrosion :

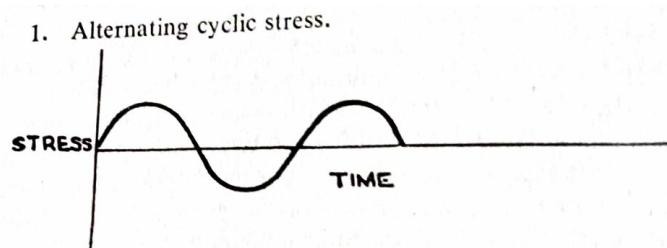
Pitting can be minimized or prevented by

1. Materials that show pitting should not be used to build the plant or equipment under consideration.
2. Addition of 2 % Mo to stainless steel increases the pitting resistance of the steel.
3. Adding inhibitors, is sometimes helpful, but may be dangerous unless attack is stopped completely.
4. Using welded butt joints instead of riveted or bolted joints in the equipment.
5. Removing wet packing materials during long shutdowns.
6. Providing uniform environments if possible.
7. Inspecting equipment and removing deposits frequently.
8. Designing vessels for complete drainage.
9. Removing solids in suspensions early in the process or plant.
10. Welding instead of rolling in tubes in tube sheets.

3.4. Corrosion Fatigue

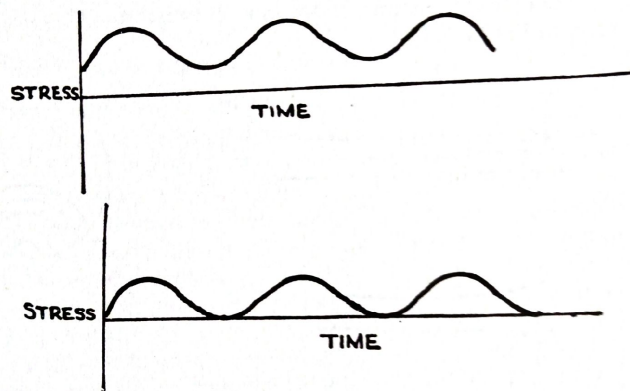
Fatigue is the tendency of a metal to fracture under repeated cyclic stresses, usually below the yield point. Corrosion fatigue is defined as the reduction of fatigue strength of material due to the presence of corrosive medium. It is the cojoint action of fatigue stress and corrosive environment. Fatigue stress must satisfy the following conditions

1. Maximum tensile stress of sufficient value.
2. Fluctuations in the applied stress.
3. Large number of cycles of applied stress (shown in following fig.)

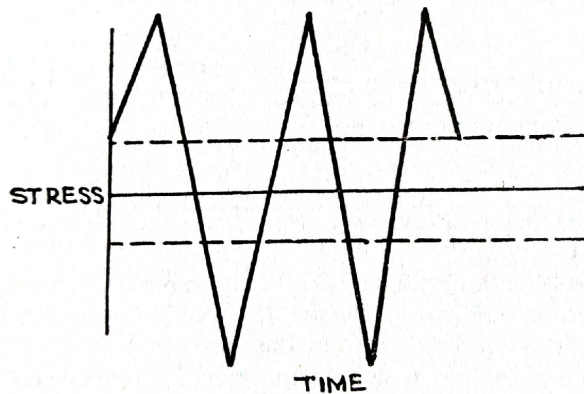


Fig, 7.5

2. Repeating cyclic stress :



3. Oscillating cyclic stress :



(Fig.3.3 Types of stress cycles)

For corrosion fatigue failure, even mildly corrosive environment is sufficient. Corrosion fatigue is most common to those environments which produce pitting attack on the surface of the material. It results in the appearance of cracks having the following characteristics:

1. It appears on the surface of the metal.
2. The cracks are usually transcrystalline, except Al alloys, fatigue cracks are intercrystalline.
3. These cracks occur usually in groups and have blunt edges.

Examples of failures due to corrosion fatigue are:

- (i) Marine propeller shaft
- (ii) Super heater tubes
- (iii) Turbines
- (iv) Boiler
- (v) Drilling pipes in oil field
- (vi) Rock drill in mining.

The fig.3.3 (a) below shows a corrosion fatigue failure of an axle.



Fig.3.3,(a) An axle failed by corrosion fatigue.

Prevention of corrosion fatigue: Corrosion fatigue can be minimised or prevented by a number of methods such as,

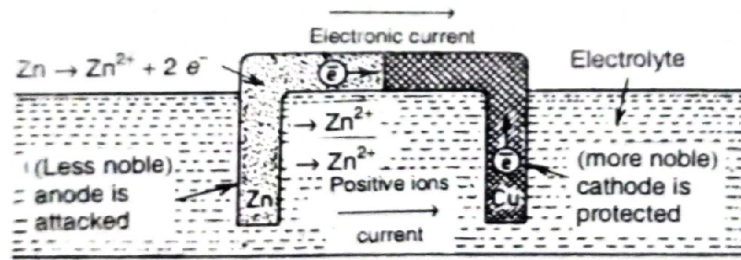
1. Reducing stress on the component ,by altering the design, by stress relieving heat treatment.
2. By adding inhibitors.
3. By electroplating of Zn, Cr, Ni, Cu and nitride.

3.5 Galvanic or Two-metal corrosion

When two dissimilar metals such as Cu and Zn are electrically connected and exposed to an electrolyte, the metal higher in emf series undergoes corrosion. This type of corrosion is known as galvanic or two- metal corrosion. In this case, Zn being higher in emf series forms the anode and attacked and get dissolved, whereas Cu, being lower in emf series acts as cathode and is unattacked. The following figure shows the scheme of formation of galvanic corrosion. The fig.3.4(a) shows an example of galvanic corrosion.



Fig.3.4 (a) An example of galvanic corrosion.



(Fig.3.4 Formation of galvanic corrosion)

The nature of the corrosive environment decides the type of cathodic reactions. In acid solution, the corrosion occurs by the hydrogen evolution process, while neutral or alkaline solutions, oxygen absorption occurs. The electron -current flows from the anodic metal(zinc) to the cathodic metal(copper). Thus it is evident that the corrosion occurs at the anodic metal , while the cathodic part is protected from attack.

Examples of galvanic corrosion are

1. Steel pipe connected in copper plumbing.
2. Steel screws in a brass marine hardware.
3. Steel propeller shaft in bronze bearing.
4. Lead-antimony solder around copper wire.

Prevention of galvanic corrosion

Galvanic corrosion can be prevented or minimised by

- 1.Avoiding direct contact between the dissimilar metals.
- 2.Rivetting or welding should be done with materials having the same chemical composition.
3. Adding inhibitors if possible to decrease aggressiveness of the environment.
4. Apply coatings with caution.
5. Avoid threaded joints for materials.

3.6 Stress Corrosion Cracking (SCC)

It is the process of destruction of metal due to the simultaneous action of corrosive environment and tensile stress. All cracking failures occurring in corrosive medium are the stress corrosion cracking. It results in the appearance of corrosion cracks. The following fig.3.5 (a) shows the stress corrosion cracking of a stainless steel pipe.



Characteristics of cracks :

- (i) These cracks appear on the surface of the metal.
- (ii) They can take different forms as shown in the following figure

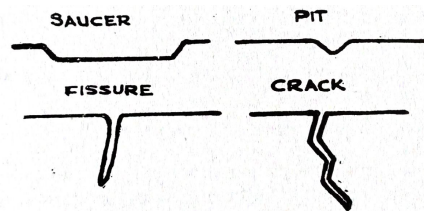


Fig.3.5. Different forms of cracks

- (iii) These cracks may be of the following types:

(a) Intergranular cracks: These cracks proceed along the grain boundaries , found in aluminium alloys,mild steels etc.

(b) Transgranular cracks: Crack propagation shows no preference for grain boundaries, found in stainless steels, brass, cast iron etc. The crack propagation may be continuous or discontinuous.

(c) Mixed type: In some materials, like Mg alloys, either type of cracks can be produced depending upon the metal structure and environment.

(iv) These cracks propagate relatively at low speeds.

(v) These cracks are narrow during early stages of cracking and wider during later stages of cracking.

(vi) These cracks may be single or branched depending upon the environment.

Factors affecting stress corrosion cracking :

The following factors affect the stress corrosion cracking

1. Stresses - Every type of stress does not cause stress corrosion. Stress must satisfy the following three conditions:

- (a) stresses should be static.
- (b) stresses should be tensile.
- (c) stresses should be of sufficient magnitude.

Increasing the stresses decreases the time before cracking occurs. There is some minimum stress required to prevent cracking. The minimum stress depends on the temperature, alloy composition and environment composition. In some cases it has been observed to be as low as about 10 % of the yield stress

2. Environments- All environments do not cause stress corrosion cracking. A list of these environments that cause SCC is given below:

Metals & Alloys	Environment
<i>Metals</i>	
Lead	Air, Solution of $\text{Pb}(\text{CH}_3\text{COO})_2$, $\text{Pb}(\text{CH}_3\text{COO})_2 + \text{HNO}_3$
Titanium	Red concentrated HNO_3 , 10% solution of HCl
Nickel	Concentrated KOH and NaOH at 130°C .
<i>Steels</i>	
Mild steel	Solution of $\text{NaOH} + \text{Na}_2\text{SiO}_3$, $\text{Cu}(\text{NO}_3)_2$, NH_4NO_3 , NaNO_3 , $\text{HCN} + \text{SnCl}_2 + \text{AsCl}_2 + \text{CHCl}_3$
Stainless steel (Fe-Cr-C, Fe-Cr-Ni-C, Fe-Cr-Ni-Mo-C)	Acid chloride solutions such as MgCl_2 and BaCl_2 , Solutions of $\text{NaCl} + \text{H}_2\text{O}_2$, Sea water, H_2S , $\text{NaOH} + \text{H}_2\text{S}$ Solution
<i>Aluminium Alloys</i>	
Al-Zn	Air
Al-Mg	Solutions of $\text{NaCl} + \text{H}_2\text{O}_2$, NaCl , Air.
Al-Mg	Sea water
Al-Cu-Mg	
Al-Mg-Zn	
Al-Zn-Cu	Solutions of NaCl , NaCl_2 , $+ \text{H}_2\text{O}_2$
<i>Magnesium Alloys</i>	
Mg-Sn	Solution of $\text{NaCl} + \text{K}_2\text{CrO}_4$, Na_2SO_4 , H_2SO_4 , Na_2CO_3 , Air.
Mg-Al	H_2SO_4 , Na_2CO_3 , Air.
Mg-Al-Mn	Solution of CH_3COOH , NaCl , KCl water, air.
<i>Copper Alloys</i>	
Cu-Zn (Brass)	Air, Amines, solutions containing nitric acid or cupric nitrate.
Cu-Zn-Sn	Air
Cu-Zn-Pb	Vapours and solution of NH_3 , Air
Cu-Sn (Bronze)	Vapours and solution of NH_3
<i>Nickel Alloys</i>	
Monel	Hydrofluoric acid, Hydrofluosilic acid
<i>Gold silver Alloys</i>	
Au-Cu-Ag	Solutions of FeCl_2
Au-Pt	Solutions of FeCl_2

3. Metallurgical factors - The susceptibility to SCC is affected by the average chemical composition, preferred orientation of grains, composition and distribution of precipitates, dislocation interactions and progress of the phase transformation.

4. Effect of temperature - The rate of corrosion increases with increase of temperature of the environment.

5. Effect of size factor - The decrease of area to volume ratio in stressed corroding specimen lead to a sharp decrease of the rate of SCC.

Good examples of SCC are

(a) Season cracking of brass parts such as condensers, tubes, boxes, gun and artillery cartridge cases . Season cracking refers to the SCC failure of brass cartridge cases. During the period of heavy rainfall, especially in the tropics, cracks were observed in the brass cartridge cases at the point where the case was crimped to the bullet. It was later found that the important environmental component in season cracking was ammonia, resulting from the decomposition of organic matter.

(b) Stress corrosion cracking of steel parts such as propeller shafts, rods of diesel engines, turbine blades, metallic cables, shafts and rods of pumps, rotors, autoclaves, parts of excavators and mining machinery, steam boilers (caustic embrittlements). Caustic

embrittlement is the brittle fracture in the presence of caustic or sodium hydroxide. The cracks are numerous and fine.

Prevention of stress corrosion cracking : Stress corrosion cracking may be reduced or prevented by the application of one or more of the following methods;

- (i) Lowering the stress below the threshold value. This may be done by annealing in the case of residual stresses, thickening the section or reducing the load. Plain carbon steels may be stress relieved at 1100 to 1200° F and austenitic stainless steels are at 1500 to 1700° F.
- (ii) Eliminating the critical environmental species by degasification, demineralisation or distillation.
- (iii) Changing the alloy is one possible recourse if neither the environment nor stress can be changed.
- (iv) Applying cathodic protection to the structure
- (v) Adding inhibitors to the system if possible. Phosphates and other organic and inorganic inhibitors may be added.
- (vi) applying coatings.
- (vii) By shot -peening or shot -blasting. It produces residual compressive stresses in the surface of the metal.

3.7. Cavitation corrosion

Cavitation corrosion or Cavitation damage is caused by the formation and collapse of vapour bubbles on or near the metal surface. Bubbles are formed in boiling liquid and collapse when pressure is increased. Cavitation damage thus occurs in systems which are subjected to rapidly alternating ranges of pressures. Liquid bubbles are formed during the low pressure cycle and collapse in high pressure cycle.. The collapse produces high stress impact which gradually remove particles of the surface and is responsible for cavitation damage. The following fig.3.6 represents a schematic of steps in cavitation corrosion.

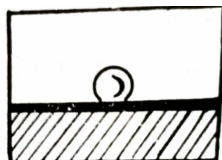


Fig.3.6 (a) A cavitation bubble forms on the protective film.



Fig.3.6 (b) The bubble collapses and destroys the film .

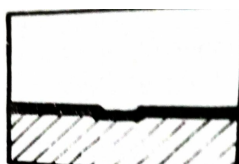


Fig.3.6 (c) The newly exposed metal surface corrodes and the film is reformed.

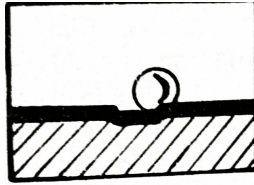


Fig.3.6 (d) A new cavitation bubble forms at the same spot.

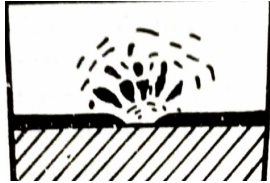


Fig.3.6 (e) The bubble collapses and destroys the film.



Fig.3.6 (f) The exposed area corrodes and the film reforms.

Cavitation corrosion occurs in hydraulic turbines ,ship propellers, pump impellers, diesel engine cylinders and other surfaces where high velocity liquid flow and pressure changes are encountered.

In actual practice, cavitation damage is the result of both mechanical and chemical action. The impact by collapse of the bubbles can cause cavitation damage due to any or combination of the following reasons:

1. Destruction of the protective film on the metal surface and thereby accelerating the corrosion process.
2. If the collapse of the bubbles produce high stresses, cavitation damage can be due to deformation and work hardening of metals.
3. Fatigue cracking of metals occurs if the collapse of the bubbles produce cyclic stresses.

Prevention of cavitation corrosion :

In general, cavitation damage can be prevented by

1. Changing the design to minimise hydrodynamic pressure differences in process flow streams.
2. Substituting more corrosion materials.
3. Resilient coatings such as rubbers, plastics, with caution.
4. Cathodic protection.
5. Alternating the environment by adding inhibitors.

3.8. Fretting corrosion

Fretting corrosion occurs at contact areas between materials under load subjected to vibration or slip. It appears as pits or grooves in the material surrounded by corrosion products. It is also called friction oxidation or wear oxidation or chafing or false brinelling (so named because the resulting pits are similar to the indentations made by a Brinell hardness tester).

The basic requirements for the occurrence of fretting corrosion are

1. The interface must be under load.
2. Vibration or repeated relative motion between the two surfaces must occur.
3. The load and relative motion of the interface must be sufficient to produce slip or deformation on the surfaces.

Examples of fretting corrosion failures are

- a) Bolted and rivetted joints.
- b) Hubs press fitted into shafts.
- c) Ball races.
- d) Control mechanism.
- e) Machine slides.
- f) Bolted tie plates on railroad rails.

The following figure shows a fretting corrosion of a tight fits subjected to vibration.

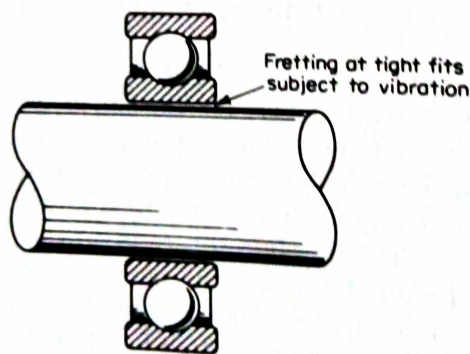


Fig.3.7 (a) Fretting corrosion of a tight fit.

The fig.3.7 (b) below shows a failure of gears and bearings due to fretting corrosion.



Fig.3.7(b)

Factors influencing fretting corrosion : The following factors influence the rate of fretting corrosion;

- (i) Amount of relative motion - The fretting corrosion increases with increase in amount of slip. But it decreases when the displacement is sufficient to allow corrosion products to escape.

- (ii) Temperature - It decreases with decrease in temperature.
- (iii) Environment - Fretting corrosion is more in dry conditions than moist conditions.
- (iv) Metallurgical factors - Soft materials are generally more susceptible to fretting corrosion than hard materials.

Prevention of fretting corrosion

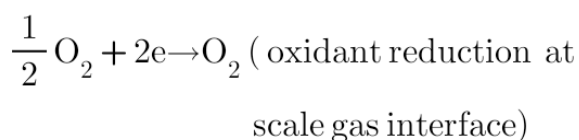
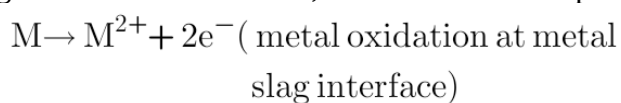
Fretting corrosion can be minimised or prevented by one or more of the following methods,

1. Lubricating with low viscosity , high tenacity oils and greases. It reduces friction between bearing surfaces and tends to exclude oxygen. Also phosphate coatings are often used in conjunction with lubricants.
2. Increasing the hardness of one or both of the coating materials. This can be accomplished by choosing a combination of hard materials and hard alloys. Also shot peening or cold working increases surface hardness.
3. Increasing friction between mating surfaces by roughing the surface.
4. Using gaskets to absorb vibration and to exclude oxygen at bearing surfaces.
5. Increasing load to reduce slip between mating surfaces.
6. Decreasing load at bearing surfaces.
7. Increasing relative motion between parts to reduce attack.

3.9. High Temperature Corrosion - Oxidation

The term oxidation refers to the chemical reaction of dry metal surface with air or oxygen in the absence of water or an aqueous phase. This is also called as dry corrosion or scaling or tarnishing. Since every metal or alloy reacts with air at ambient temperatures, oxidation resistance must be considered in most of the engineering applications. Oxidation limits the use of metals in high temperature power plants. Certain applications where oxidation should be considered are in design of gas turbines, rocket engines, furnaces and high temperature petrochemical processes.

Electrochemical aspects of oxidation - Oxidation by gaseous oxygen is an electrochemical process. It is not simply the chemical combination of metal and oxygen on a molecular scale, but consists of two partial processes.



The most important parameter of metal oxidation is the reaction rate and is usually measured as weight gain per unit area. The various empirical rate laws applicable for the oxidation of metals are described below: **x** be the thickness of the film and **t** be the time

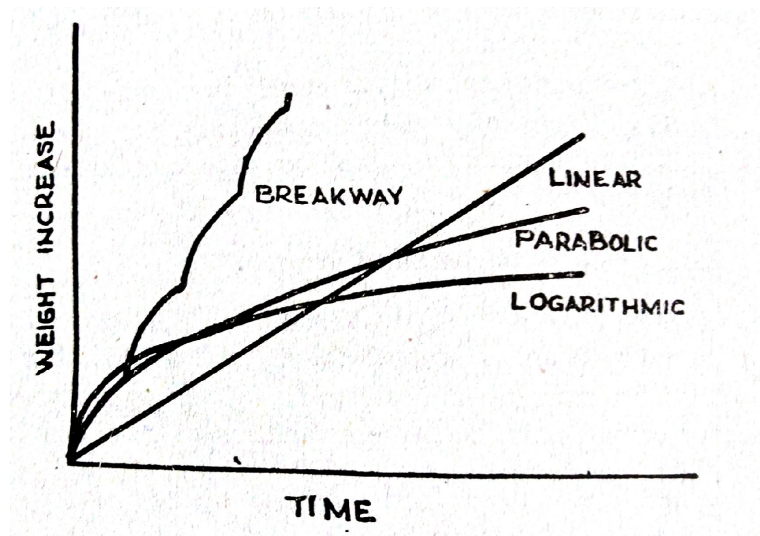


Fig.3.8 Empirical rate laws during oxidation.

1. **Linear Law** ($x \propto t$) - The linear law applies to the initial stage of oxidation before the film is thick enough to be protective. Na, K, Ta and Columbium oxidise linearly.
2. **Logarithmic Law** ($x \propto \log t$) - The logarithmic law applies mainly to highly protective thin films formed at low temperatures, ($< 1000^{\circ}\text{C}$) . Al, Cu, Fe and some other metals oxidise in this manner.
3. **Parabolic Law** ($x \propto t^{1/2}$) - The parabolic law applies at intermediate temperature. Iron oxidises in this manner between 200 to 400° C.
4. **Break away effects** - Break away effects are observed when something happens to the film, such as cracking or flaking which reduces its thickness. When the oxide is brittle, discontinuous break away curve is obtained.

Prevention of High Temperature Corrosion

High temperature corrosion or oxidation can be prevented or minimised by

1. Using highly oxidation resistant materials. The oxidation resistance of the metal can be improved by adding suitable alloying elements by Hauffe's valency rule. According to this rule, if the oxide is deficient in metal atoms, add an alloying element of lower valency to reduce the number of vacancies present. If the oxide contains an excess of metal atoms, add an alloy element of higher valency.
2. By selective oxidation - Noble metals such as silver or copper can be protected by selective oxidation. In this case, 1 % of a highly reactive metal such as Al is dissolved in the basis metal, which is then carefully oxidised in an atmosphere too weak to oxidise more than the alloy metal and a stable film is formed. e.g. Al_2O_3 formed on a sterling silver (92.5 % Ag, 6.5 % Cu, 1 % Al) to give a tarnish resistant silver.
3. Larger alloy additions are made to iron and steel to gain oxidation resistance Al and Si both give very protective oxide film. The most common addition is chromium.
4. Coating the object with suitable material such as gold plating, chromium plating etc.
5. Coating ceramics such as silicides, borides, Al_2O_3 , Cr_2O_3 etc.

3.10 . Stray Current Corrosion

Stray current corrosion refers to corrosion resulting from stray current - the current flowing through paths other than the intended circuit. It is the extraneous direct currents in the earth. The stray currents are due to current leakage from:

1. DC rail transit system
2. Cathodic protection system
3. Electrical welding machines
4. Trolley tracks.
5. Pipeline and tanks

After leaking it flows through the earth or through metallic structure embedded in it . Corrosion occurs at points where current leaves the metallic structure. It is a dynamic and transient phenomenon. Corrosion only occurs at the point of discharge. At the point of entry and along the entire system that carries the stray current, there is no corrosion. At the point of entry, stray current provides certain degrees of cathodic protection.

All metallic structures buried or immersed are susceptible to stray current corrosion. The following fig.3.9 shows the stray current corrosion resulting from cathodic protection.

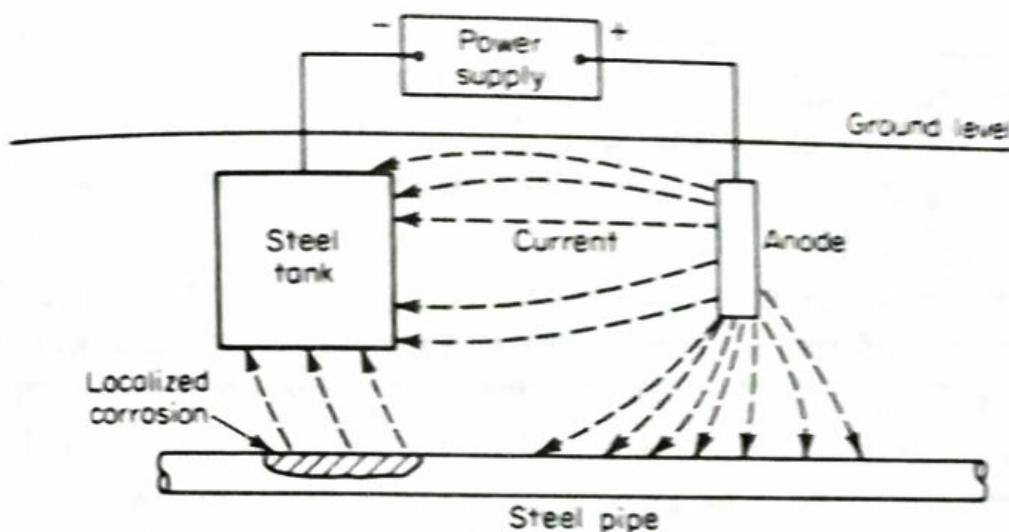


Fig.3.9. Stray current corrosion resulting from cathodic protection.

Prevention of stray current corrosion

Stray current corrosion can be prevented or minimized by the following measures;

1. Identify the source of stray current.
2. Stop the leakage from the intended circuit by maintaining good electrical connections and insulations.
3. Install impressed cathodic protection system to offset the effect of stray current.
4. By proper design as shown in fig.10. below.

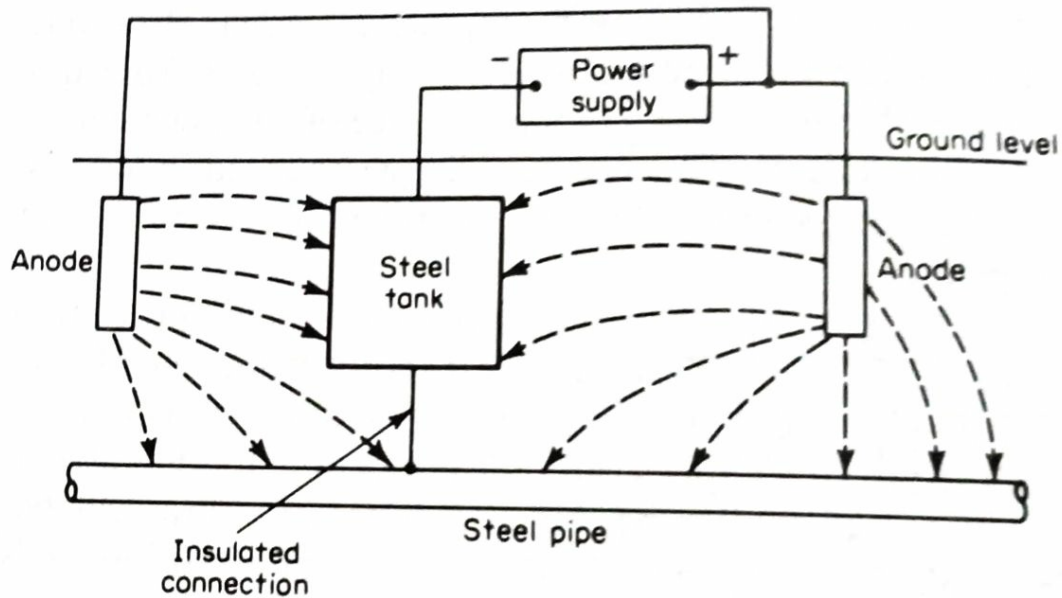


Fig.3.10. prevention of stray current corrosion by proper design.

3.11. Erosion corrosion

Erosion corrosion results by the combined effect of the abrading action of vapours, gases and liquids and the mechanical rubbing action of solids over the surface of the metals. Metal is removed from the surface as dissolved ions or it forms solid corrosion products that are mechanically swept from the metal surfaces. It is characterized in appearance by grooves, gullies, waves, rounded holes and valleys. The following fig.3.11. shows an erosion corrosion of a condenser tube wall handling water.

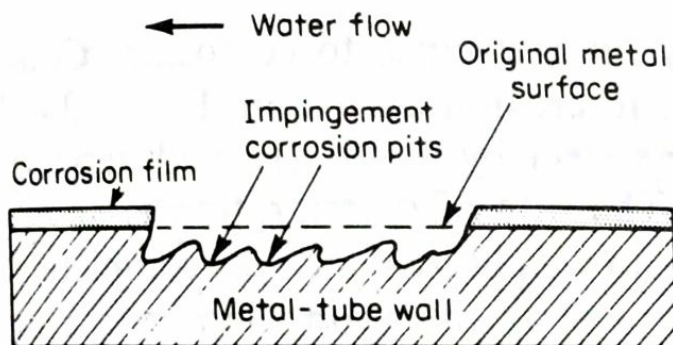


Fig.3.11 Erosion corrosion of condenser tube wall



Fig.3.12. Erosion corrosion of a pipeline.

Most metals and alloys are susceptible to erosion corrosion , for example, Al, Pb and stainless steels. Metals that are soft and readily damaged or worn mechanically such as Cu and Pb are quite susceptible to erosion corrosion. The corrosive mediums that cause erosion corrosion are gases, aqueous solutions, organic systems and liquid metals. For example, hot gases may oxidise a metal and then at high velocity blow off an otherwise protective scale. Solids suspension in liquids (slurries) are particularly destructive from the standpoint of erosion corrosion. All types of equipments exposed to moving fluids are subjected to erosion corrosion. Some of them are piping systems, particularly bends, elbows, tees, valves, pumps, blowers, centrifugals, propellers, impellers, agitators, agitated vessels, heat exchanger tubing such as heaters and condensers, measuring devices such as orifices, turbine blades, nozzles, ducts, and vapour lines, scrapers, cutters, wear plates, grinders, mills, baffles and equipments subjected to spray.

Prevention of erosion corrosion

Erosion corrosion can be combated or minimized by

1. The use of materials with better resistance to erosion corrosion.
2. The use of better design of equipments.
3. The alteration of the environment - Deaeration and addition of inhibitors.
4. The application of coatings.
5. The application of cathodic protection.

3.12. Uniform corrosion

Uniform corrosion or uniform attack is the most common form of corrosion. It is normally characterized by a chemical or electrochemical reaction that proceeds uniformly over the entire exposed surface or over a large area. The metal becomes thinner and eventually fails. This type of corrosion occurs when the whole surface of the metal is corroded to the same degree and when the metal surface and the environment are uniform. This unlocalized attack may start in its initial phase at certain areas and spreads over the whole surface of the metal gradually, as a result, the whole surface in course of time is uniformly corroded. Examples of uniform corrosion are;

1. A piece of steel or zinc immersed in dilute sulphuric acid will normally dissolve at a uniform rate over its entire surface.
2. Action of metals such as Al, Zn, Fe and Pb on atmospheric air shows a uniform attack over the entire surface of the metal.

Prevention of uniform corrosion

Uniform corrosion can be prevented or reduced by

1. Selecting proper materials, including coatings.
2. Use of inhibitors.
3. Cathodic protection.

3.13. Underground corrosion

Underground corrosion or soil corrosion is a geologic hazard that affects buried metals and concrete that is in direct contact with soil or rockbed. Soil corrosion is a complex phenomenon with a multitude of variables involved. Pitting corrosion and stress corrosion cracking are the result of soil corrosion, which leads to underground oil and gas transmission pipeline failures. But there are some basic concepts that are useful in understanding the process.

Underground corrosion is electrochemical in nature. The common indicators of a soil's tendency to corrode ferrous metals are electrical resistivity, chloride content and pH level. Corrosion soils contain chemical constituents that can react with construction materials such as concrete and ferrous materials, which may damage foundations and buried pipelines. The following fig.3.13 shows a pipeline system that corroded by underground corrosion.



Fig.3.13. underground corrosion of pipeline.

The electrochemical corrosion process that takes place on metal surfaces in soils occurs in the groundwater that is in contact with the corroding structure. Both the soil and climate influence the underground composition.

Factors affecting soil corrosion

The following factors affect the soil corrosion:

1. Porosity (aeration)
2. Electrical conductivity or resistivity
3. Dissolved salts
4. Moisture
5. pH

Each of these variables may affect the anodic or cathodic polarization characteristics of a metal in soil. The most corrosive soils have high content of moisture, electrical conductivity, acidity and dissolved salts.

Prevention of underground corrosion

Underground corrosion can be controlled by

1. Using organic and inorganic coatings
2. Applying metallic coatings
3. Alteration of soil
4. Cathodic protection.

3.14. Crevice corrosion

It is an intensive localized attack that occurs within crevices and other shielded areas on metal surfaces exposed to corrosive environments. This type of corrosion is usually associated with small volume of stagnant solution caused by holes, gasket surfaces, lap joints, surface deposits, and crevices under bolt and rivet heads. As a result, this form of corrosion is called crevice corrosion or deposit or gasket corrosion.

Examples of deposits that may produce crevice corrosion are sand, dirt, corrosion products and other solids. The deposit acts as a shield and creates a stagnant condition. Contact between metal and nonmetallic surfaces can cause crevice corrosion as in case of a gasket. Wood, plastics, rubber, glass, concrete, asbestos, wax and fabrics are examples of materials that can cause this type of corrosion. Stainless steels are particularly susceptible to crevice corrosion. The figure given below shows a crevice corrosion on a stainless steel pipe flange.



Fig.3.14 Crevice corrosion on a stainless steel pipe flange.

Prevention of crevice corrosion

Crevice corrosion can be prevented or minimized by the following methods or procedures:

1. Use welded butt joints instead of rivetted or bolted joints.
2. Design vessels for complete drainage. Avoid sharp corners and stagnant areas.
3. Remove wet packing materials during long shut downs.
4. Weld instead of rolling in tubes in tube sheets.
5. Use solid non absorbent gaskets such as teflon.
6. Remove solid in suspension early in the process.
7. Inspect equipment and remove deposits frequently.

Control and Prevention of Corrosion

4.0. Control and prevention of corrosion

Since the types corrosion are so numerous and the conditions under which corrosion occurs are so extremely varied, many methods of diverse are now used to prevent or minimise corrosion problems. The method or combination of methods used to deal with corrosion problems are largely dependent on economic considerations and practical situations where the methods will be applied.

The various protective measures to combat or minimise corrosion can be classified under the following headings:

1. Control of the physical, chemical and mechanical characteristics of the metals and alloys.
2. Control of the environment.
3. Control of the external source of electric potential.

4.1. Control of the physical, chemical and mechanical characteristics of metals and alloys :

The various methods under above heading are given below:

1. Protective coatings
2. Purification of metals
3. Heat treatment
4. Alloying
5. Change in design

4.1.1 Protective coatings :

Both metallic and non-metallic coatings are applied to prevent corrosion and have the following characteristics:

- (i) Good corrosion resistance against the medium with which it comes in contact.
- (ii) Perfect adherence to the underlying metals.
- (iii) Continuous, so as to cover the surface completely.

(A) Metallic coatings -

The metal film coated on the surface of the base metal may act to prevent corrosion of the base metal in two ways:

- (i) Cathodic coatings - It provides a physical barrier between the base metal and corrosion media. Exp. Coating of gold, Aluminium, Chromium on iron.
- (ii) Anodic coatings - It provides a better solvating cage or more anodic surfaces than the base metal. Exp. Coatings of Zn, Al, Cd on steel.

Advantages of metallic coatings over other coatings :

1. More durable than non metallic coatings.
2. More decorative.

3. Best shielding against corrosion.

Methods of applying metallic coatings:

Metallic coatings can be applied by various methods which are briefly described below:

(a) Hot dipping: - This method is used for tinning and galvanizing of various steel sheets. The object is dipped or immersed in molten bath of low m.p. metals like tin, zinc, lead and aluminium. Although this method is simple but many complications are involved such as uneven coating, control of proper thickness is difficult etc.

(b) Metal spraying: - In this method the liquid metal usually low m.p. metals and alloys are sprayed over the base metal. The surface is grit blasted and the liquid metal is sprayed over it by a pistol as shown in fig.4.1 below.



Fig.4.1 metal spray by pistol.

(c) Cladding : - This method is used for coating copper on steel plates or lead on copper plates etc. It consists of rolling the metal over the base metal. It is only for sheets or plates, as shown below

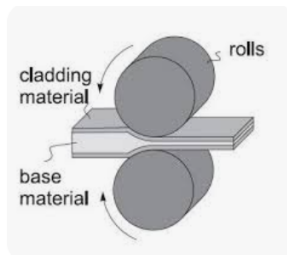
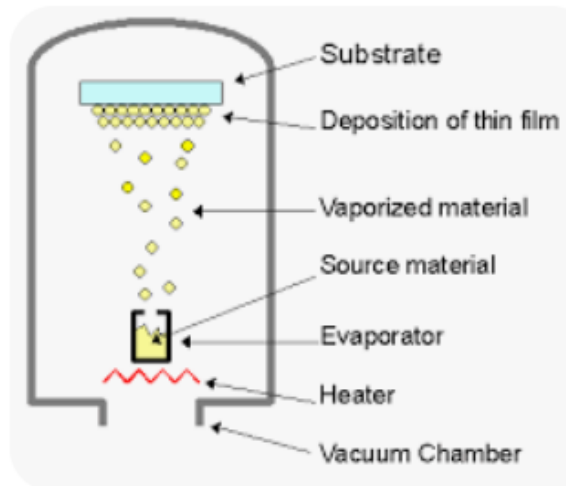


Fig.4.2 Cladding

(d) High temperature diffusion: - Diffusion coatings involve heat treatment to cause alloy formation by diffusion of one metal into the other. This is also known as surface alloying. Parts to be coated are placed in solid materials or exposed to gaseous environments containing the metal that forms the coating. For example, sheradizing

(Zn), chromizing(Cr) , alonizing(Al) etc.

(e) Vacuum deposition: This is accomplished in a high vacuum chamber. The coating metal is vaporized by heating electrically and the vapour deposits on the parts to be coated. Exp. deposition of aluminium on steel parts. The fig.4.3 below shows the process of vacuum deposition.



(f) Electroplating: The object to be coated is cleaned and washed and then dipped into suitable bath(salt of coating metal or alloy) . Another plate of a coating metal is also dipped in it . The plates are connected to a DC power supply making the objects to be plated as cathode. Fig.4.4 shows the process of electroplating.

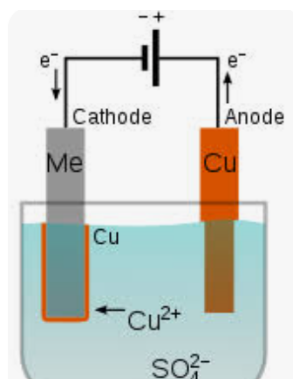


Fig.4.4. process of electroplating

(B) Non metallic coatings -

Non metallic coatings applied to prevent corrosion are of two types:

(a) *Inorganic coatings*: - The principal inorganic coatings for metals are

(i) Vitreous enamels: They form hard glass outside layer and protect by acting as an efficient barrier to the corrosive environment.

(ii) Portland cement coating: They can act a diffusion barrier to the corrosive environment. They give adequate protection to steel.

(iii) Conversion coating: These coatings are formed by reaction with the metal surface and are of several types such as phosphate coating from acid phosphates on steels, oxide coatings on steel and aluminium formed by the reaction with oxygen and water or steam. Oxide coatings provide moderate barrier which is quite effective in moderately corrosive environment.

(b) Organic coatings

Organic coatings are inert organic barriers applied on the surface of the materials for both corrosion protection and decoration. Organic coatings include varnishes, paints, enamels (dispersion of pigments in a varnish or resin), and lacquers (a solvent solution of resin and plasticizers with or without pigments dispersed throughout). Organic coatings are used under conditions in which the corrosion rate of an unprotected metal is less than 0.5 inch per year.

4.1.2. Purification of metals

Corrosion resistance of a given metal may be improved by increasing the purity of metal. Extremely pure metals corrode at a very slow rate owing to their hydrogen over voltage. The rate of corrosion increases rapidly with decreasing the purity of base metal. The following table shows how the rate of corrosion increases with decreasing the purity of aluminium in 20 % HCl.

Table -4.1

<u>Purity of Al %.</u>	<u>Loss of weight (gm/day)</u>
99.998	6
99.99	112
99.98	3600
99.97	6500
99.2	190000

4.1.3. Heat treatment

Corrosion resistance of metals and alloys can be improved by proper heat treatment by altering the microstructure, nature, magnitude of internal stresses for changing protective properties of oxide film on the metal surface. The following heat treatment processes are carried out for improving the corrosion resistance of the metals and alloys:

(i) *Annealing*: It is carried out to homogenize the microstructure, composition, and reduce the residual stresses thereby improving the corrosion resistance of the metal.

(ii) *Hardening and tempering*: Hardening treatment increases the corrosion resistance of steel because it contains a single phase martensite. Similarly tempering at low temperatures forms many galvanic cells of ferrite and carbides, resulting in increase in corrosion rate , but tempering at high temperatures, the carbides agglomerate causing reduction in galvanic cells thereby improving the corrosion resistance.

(iii) *Precipitation hardening* : The age hardenable alloys in solution heat treated condition shows better corrosion resistance than that of in aged condition. This is due to the increase in galvanic cell with precipitation. Overageing, however decrease the corrosion rate due to the agglomeration of the particles which results in decrease in number of galvanic cells as in fig 4.5 below.

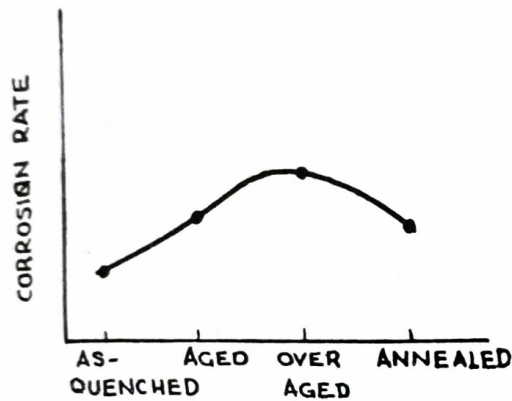


Fig. 4.5. Effect of ageing on rate of corrosion.

4.1.4. Alloying

Corrosion resistance of most commercial steels can be increased by alloying them with suitable alloying elements. For maximum corrosion resistance the alloy should form solid solution. Exp. Addition of chromium and nickel with iron, nickel with copper can increase the corrosion resistance of iron and copper respectively. Alloying elements may increase the corrosion resistance due to any of the following reasons:

- (i) Alloying may alter the structure of the metal by solid solution in such a way as to reduce Critical Current for passivation. The improvement in corrosion resistance of iron and copper by the addition of chromium and nickel respectively is attributed to the above reason.
- (ii) The alloying may raise the nobility of the solution thereby reducing the driving e.m.f. in the corrosion cell.
- (iii) Alloying may give rise to more protective corrosion product e. g. additions of relatively small amount of Cu, Cr, Ni to steels.
- (iv) The alloying elements may increase the corrosion resistance by decreasing the mobility of the corrosive ion. Addition of Sn to Zr increases the corrosion resistance by neutralizing the vacancy generated by nitrogen thereby reducing the mobility of oxygen ions in the oxide film on the surface.
- (v) The corrosion resistance can also increase by decreasing the areas of cathodes and increasing the areas of anodes thereby reducing the anodic current. Nickel addition to cast iron decreases the areas of cathodic inclusions due to decrease in percentage of carbon, resulting in increase of corrosion resistance.

4.1.5. Change in design

Corrosion rate can be reduced by proper design and fabrication. The design should be such so as to maintain uniform conditions as far as possible throughout. For better corrosion resistance the following points are to be considered:

(i) The use of two dissimilar metal contact should be avoided, because in the presence of an electrolyte such contact may result in galvanic corrosion. If their use is essential, they should be as close as possible in galvanic series.

(ii) The design should avoid the presence of crevices between adjacent parts of the structure and to avoid conditions such as rapidly moving water, the accumulation of solid etc.

(iii) Dissimilar materials should be insulated.

(iv) The design should be as to avoid the excessive stress concentration. This can be avoided by proper fabrication and design. Some examples of proper design for reducing stress concentration are given in fig.4.6. below.

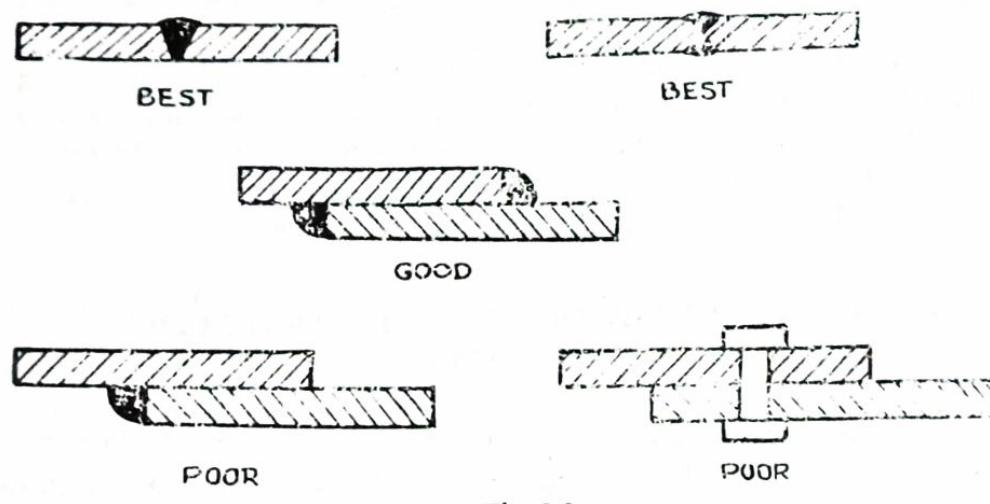


Fig. 4.6 Proper design to reduce stress concentration

(v) The design should be such as to provide uniform temperature gradient.

(vi) Wall thickness in pipes, tankss, should be designed so as to make allowances for reduction in thickness due to uniform corrosion.

4.2. Control of the environment

Corrosive environment plays the most important part in all corrosion processes. If, therefore, an environment can be created so as to make the materials less corrosive they can be saved to a great extent by harmful effects of corrosion.

Altering the environment provides a versatile means for reducing corrosion. Corrosive environment can be modified by the following three ways:

1. Altering environmental variables such as temperature, pressure, concentration, velocity, pH etc.
2. Elimination of corrosive ingredients such as humidity, oxygen, oxidising agents,

solid contaminants etc.

3. Introduction of inhibitors.

4.2.1. Alteration of environment

(i) Alteration in temperature: In most cases, lowering the temperature of the environment reduces the corrosion rate. The degree of reduction depends upon the type of environment, metals, alloys. For example, the corrosion rate is high in cases such as 18 Cr- 8 Ni steel in nitric acid, monel in hydrochloric acid and nickel in sodium hydroxide (curve A, fig.4.7) .

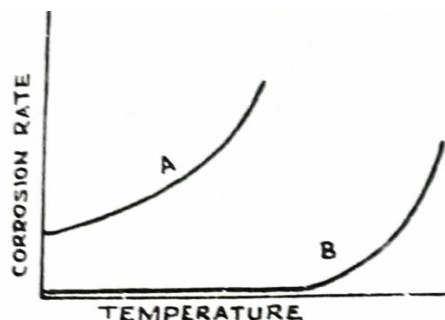


Fig.4.7 Effect of temperature on corrosion rate

However , under certain conditions temperature changes have a little effect on corrosion rate. For example, the reduction is less in cases such as 18 Cr- 8 Ni in sulphuric acid, Nickel in hydrofluoric acid, and iron in hydrochloric acid.(Curve B, fig.4.7)

In certain cases, lowering in temperature increases the corrosion rate. For example, boiling sea water is less corrosive than hot sea water at 65 °C.

(ii) Alteration in concentration: In most cases, lowering the concentration of corrosive reduces the corrosion rate. There can be a concentration below which corrosion rate remains constant. Exp. Ni in NaOH and 18 Cr- 8 Ni in nitric acid (Curve A ,fig.4.8) . In some cases such as Al in acetic acid or nitric acid, 18 Cr - 8 Ni in sulphuric acid and iron in sulphuric acid.(Curve B). The corrosion rate is higher at lower concentration and minimum at higher concentration.

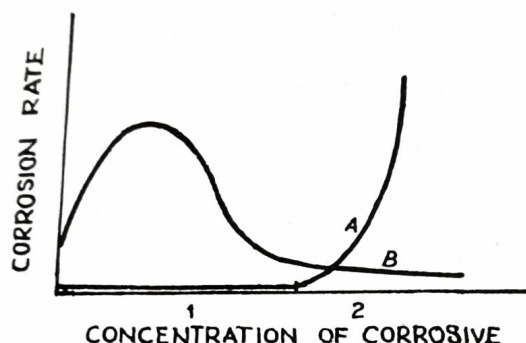


Fig.4.8. Effect of concentration on corrosion rate.

(iii) Alteration in velocity: The effects of velocity on corrosion rate depends on the characteristics of the metal and the environment to which it is exposed. Velocity of the

environment may decrease or increase the corrosion rate. In most cases, decrease in velocity reduces corrosion rate. Decrease in velocity to zero (stagnation) can increase corrosion rate. During stagnation period, corrosion rate is increased due to settling of suspended matter. In cases where the corrosion process is under diffusion control and the metal is readily passivated, increase in velocity reduces the corrosion rate. Fig.4.9.

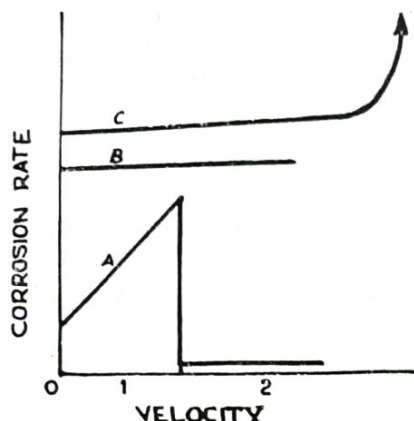


Fig.4.9 Effect of velocity on corrosion rate.

(iv) Alteration in pH value: High pH value of environment usually reduces the corrosion of iron and steel.

4.2.2 Elimination of corrosive ingredients

(i) Dehumidification: It is the process of reducing environment moisture to such an extent, the amount of water condensed on metal surface is too negligible to cause corrosion. At a given temperature, there is a critical humidity for many metals such as steel, Cu, Zn and Ni. If the relative humidity is kept below 30 % , corrosion of most metals will be negligible. In most cases, humidity is lowered below 30 %.

Methods of dehumidification:

- By use of silica gel, activated alumina and lime which absorbs water.
- Extraction of moisture from air by condensation.
- By raising the temperature of air.

(ii) Elimination of solid contaminants: Dissolved solid contaminants in water increases the corrosion rate, because they may increase the electrical conductivity. This will speed up the electrode reactions and hence corrosion rate. Dissolved ions can penetrate the protective coating formed by corrosion products.

(iii) Elimination of oxygen and oxidation agents: Corrosion rate can be reduced in certain cases by reducing the concentration of oxygen and oxidising agents from the environment. The following methods are available for this purpose:

1. By the adjustment of temperature and pressure together with mechanical agitation so that dissolved gases are expelled from the solution.
2. By the addition of certain chemical reagents such as sodium sulphite, hydrazine etc.

4.2.3. Introduction of inhibitors

An inhibitor is a substance which when added in small amounts to an environment effectively decreases or retards the corrosion rate. In a sense, an inhibitor can be considered as a retarding catalyst.

Inhibitors are used in liquid media, gaseous media as well as to solid and semi-solid materials such as paint films, packing materials and protective greases.

Mechanism of inhibition : Inhibitors can prevent corrosion by two mechanisms as

1. By formation of protective layer on the metal surface, and
2. By reducing the corrosiveness of the environment towards the metal.

Classification of inhibitors

Inhibitors can be classified mainly into three types, as

- (A) Filming inhibitors such as
 - (i) Anodic inhibitors
 - (ii) Cathodic inhibitors
 - and (iii) Mixed type (anodic and cathodic)
- (B) Adsorption inhibitors
- (C) Vapour phase inhibitors.

(A) Filming inhibitors: The inhibitors which form a barrier isolating the metal from solution are called filming inhibitors. Since aqueous corrosion is electrochemical in nature, inhibitive action of any substance is the result of prevention and control of anodic and cathodic reactions. Inhibitors that suppress the anodic reaction or metal dissolution, are called anodic inhibitors while that suppress the cathodic reaction are called cathodic inhibitors.

(i) Anodic inhibitors: These inhibitors seal off the anodic regions, where the metal cations are formed, by forming oxide film. These are called dangerous inhibitors if used in insufficient quantity.

Examples of anodic inhibitors are oxidising substances such as chromates, phosphates, silicates, nitrates, benzoates, tungstates etc. They precipitate the anodically dissolved metal thus lead to the formation of adherent protective layer.

(ii) Cathodic inhibitors : The cathodic inhibitors suppress the cathodic reactions. The cathodic reactions are suppressed by;

1. Slowing down the diffusion of hydrated ion to the cathode.
2. Increasing the discharge potential of hydrogen.
3. Eliminating oxygen from solution.
4. Delaying the diffusion of dissolved oxygen towards cathode by forming an obstructing layer.

The first two methods are applied to acid solution and last two for neutral solution.

Examples of cathodic inhibitors are ;

Organic inhibitors such as amines, heterocyclic nitrogen compounds , sulphides, heavy metal soaps, Inorganic inhibitors are bicarbonates, and phosphates.

Cathodic inhibitors are less effective than anodic inhibitors because in this case the mechanism of corrosion prevention is indirect whereas in anodic inhibitors the mechanism of corrosion prevention is direct.

(iii) Mixed type : These inhibitors suppress both cathodic and anodic reactions. Benzoate and Thiourea are the examples of this type.

(B) Adsorption inhibitors

Adsorption inhibitors are the surface active addition agents and represent the largest class of inhibiting substances. In general, these are organic compounds which adsorb on the metal surface and suppress metal dissolution and reduction reactions. In most cases, it appears that adsorption inhibitors affect both the anodic and cathodic processes, although in many cases, the effect is unequal. Typical of this class of inhibitors are aliphatic and aromatic amines, thiourea and aldehydes.

(C) Vapour phase inhibitors

These are very similar to the organic adsorption type inhibitors and possess a very high vapour pressure and the vapour of which has corrosion inhibiting properties. These inhibitors are usually only effective if used in closed spaces. Most effective vapour phase inhibitors are;

1. *Dicyclohexyl ammonium nitrite* (v.p.- 0.0001 mm Hg at 25 °C) .

This is used to inhibit the corrosion of steel, however it increases the corrosion rate of Zn, Mg, and Cd.

2. *Cyclohexylamine* (v.p.- 0.4 mm Hg at 25°C).

It reduces the corrosion rate of steel, aluminium solder, and Zn, but increases the corrosion rate of copper, brass and magnesium.

Advantages of vapour phase inhibitors

1. Easily applicable to articles.
2. No need of removal of oil or grease film before application.

Disadvantages of vapour phase inhibitors

1. It accelerates the corrosion rate of certain non ferrous metals.
2. It requires effective sealing of package against the loss of inhibiting vapour.
3. It discolours certain plastics.

Applications of inhibitors

Inhibitors are used for protecting ferrous and non ferrous metals such as aluminum, zinc, tin, and copper and their alloys.

Some of the typical applications are given below:

1. Air conditioners : Addition of a mixture of sodium dicarbonate and sodium carbonate or NaOH in very small quantities retard the corrosion rate..
2. Iron pillar: It was found that the Iron pillar was protected from corrosion by the addition of inhibitors like phosphate and tannels.
3. Steam condensate lines: Corrosion of steam condensate lines in power plants can be minimised by the addition of morpholine.
4. Corrosion of copper in potassium persulfate solution can be inhibited by the addition of salicylaldehyde, formaldehyde and cyclohexanone.
5. Corrosion of aluminium alloys are inhibited by the addition of dextrine and hexamethyltetramine.

Limitations of inhibitors

1. It is not possible to add inhibitors to all corrosive systems because they can contaminate the environment.
2. Certain inhibitors are toxic in nature. They can not be used for protecting food utensils etc.
3. Most of the inhibitors can not be used at high temperatures.
4. Inhibitors are only used in closed systems.
5. Anodic inhibitors are regarded as dangerous inhibitors if used in insufficient quantity.

4.3. Control of external source of electric potential

Corrosion in aqueous environments is primarily electrochemical in nature which can be controlled by application of source of external electric potential. This include two methods as:

1. Cathodic protection method
2. Anodic protection in method,

4.3.1 Corrosion prevention by cathodic protection

It is the minimization or prevention of corrosion of metallic surface by making it cathodic with respect to environment. Cathodic protection is achieved by supplying electrons to the metal structure to be protected.

For example, a metal M is in an acid environment. Electrochemical reactions occurring are-



These reactions indicate, the addition of electrons to the metal structure will tend to suppress metal dissolution and increase the rate of hydrogen evolution.

Cathodic protection is achieved by supplying electrons either from a

- (a) Galvanic or Sacrificial anode, or by
- (b) Impressed current

(a) Cathodic protection by Galvanic or sacrificial anode method

In this method, the metallic structure is made cathode by connecting it with galvanic anodes which is more electropositive than the metal structure to be protected. When it is connected to the structure, it becomes anode and sacrificially protects the structure.

Fig.4.10 shows such installation.

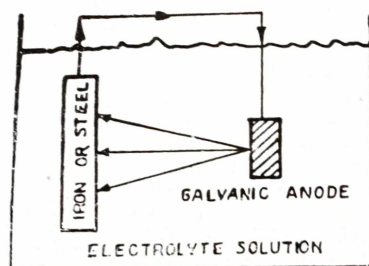


Fig.4.10 Cathodic protection by galvanic or sacrificial anode.

Factors affecting protection by galvanic anode method:

The following factors must be taken into consideration;

1. Factors to be considered in choosing anodes include driving voltage, capacity and cost. The following materials are generally used.

(a) Magnesium and its alloys : Magnesium is widely used as sacrificial anode. Its efficiency is only about 50 %, but it has high negative potential ($E^\circ = 2.3 \text{ V}$) which provides high current output. Its operating efficiency can be raised by the addition of 6 % Al, 3 % Zn and 0.2 % Mn.

(b) Zinc and its alloys It is also used as sacrificial anode. It has potential of $E^\circ = 0.8 \text{ V}$. The current output of a Zn anode is lower than that of a Mg anode of the same size. At low current output the efficiency of zinc is higher than that of a magnesium, which imparts long life to anode.

(c) Aluminium and its alloys: Aluminium and its alloys are used for sacrificial anode.

2. *Geometry of anode:* Anode can be cylindrical, plate or variable type. The cylindrical type has a relatively low output but a long operating life. The plate type has a large surface area and therefore large output in relation to mass. The variable output anode has a relatively high output for a very short time.

3. *Number and spacing of anodes:* These depend on the system to be protected. The ideal arrangement should have number of anodes in such a position that all the steel work is equidistant from it so that protective current spreads uniformly.

Advantages of galvanic anode method : The main advantages of this method are as follows:

1. No external power supply necessary.
2. Minimum maintenance cost after installation.
3. Low installation cost
4. More efficient utilisation of protective coating.

Disadvantages of galvanic anode method: The main disadvantages are;

1. Limited driving potential and current output.
2. Soil resistivity limitations.
3. Not applicable to large objects or poorly coated pipes.
4. There is some interference in parallel or multiple installations.

(b) Cathodic protection by impressed current method

In this method, metallic structure to be protected is made cathode with the use of impressed current. It is done by connecting the negative terminal of the external power supply source to the metallic structure and positive to an inert anode.

This is shown in fig.4.11 below.

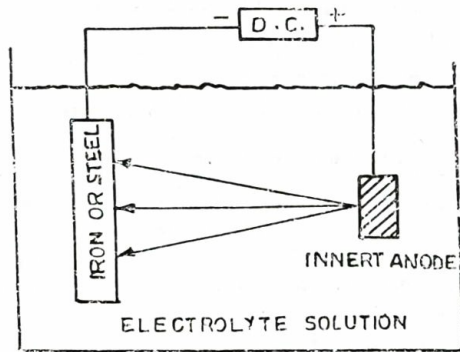


Fig.4.11 Cathodic protection by impressed current.

In general, power is taken from main supplies, transformed to required voltage and rectified. Self-contained transformer rectifier units are normally employed. Inert anode can be made of scrap steel, aluminium, graphite and platinum group metals.

Advantages of impressed current method

The main advantages of impressed current method are as follows:

1. Larger driving voltage.
2. Larger flexibility of control.
3. Applicable to large objects.
4. Uncoated parts can be protected.

Disadvantages of impressed current method

The main disadvantages of this method are as follows:

1. Larger installation cost.
2. Higher maintenance cost.
3. Interference with parallel currents.

Applications of cathodic protection

Various types of electrochemical corrosion such as aqueous corrosion, erosion corrosion, cavitation corrosion, corrosion fatigue and stress corrosion cracking are effectively minimised or prevented by cathodic protection method. Some of the typical applications are given below:

1. Protection of pipelines : Underground pipelines are protected by both galvanic anode method and impressed current method. Fig.4.12(a).

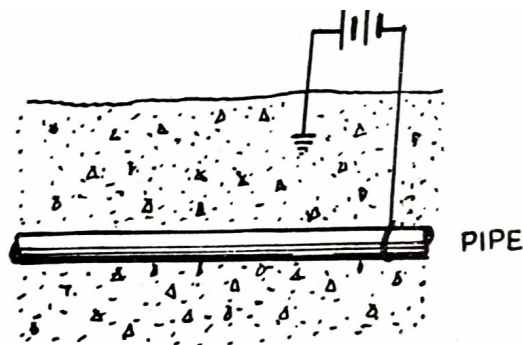


Fig.4.12((a) Cathodic protection of underground pipe by impressed current.

The choice between galvanic anode and impressed current generally depends upon soil resistivity. The coated structures are economically protected by cathodic protection.. The fig.4.12(b) below shows the protection of underground pipe by galvanic anode.

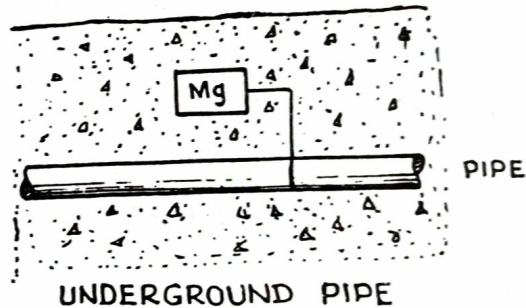


Fig.4.12(b) Cathodic protection of underground pipe with galvanic anode.

2. Protection of underground cable sheaths : Cable sheaths of lead and aluminium are protected by cathodic protection.

3. Protection of chemical equipment: Various liquid containers such as storage tanks, heat exchangers, condensers etc. are protected by cathodic protection. Some of the equipments protected by cathodic protection are given below:

- (a) Lead pipe, coils in barium chloride solution is protected by using Zn anodes.
- (b) Copper and Hastelloy components handling 10 % HCl at 60°C is protected by using lead anodes.
- (c) Copper heating steam coils immersed in zinc chloride and ammonium chloride are protected by using zinc anodes.
- (d) Steel equipments in chlorinated water, conc. brine solution are protected by using magnesium anode.
- (e) Mild steel in pure 73 % caustic soda plus 0.3 % sodium chloride at 100°C is protected by impressed current method.
- (f) Copper steam coils in ammonium chloride solution is protected by impressed current using lead as inert anode.

5. Steel structures exposed to seawater are protected by cathodic protection method.

Limitations of cathodic protection method

The following are the limitations of cathodic protection:

- 1. If cathodic polarization is too great, certain metals such as lead and tin are attacked by gasification.
- 2. An applied cathodic current may lead to reducing conditions in certain passive alloys such as stainless steel which can destroy the passivity.
- 3. When there are neighbouring buried structures not in direct electrical connection with the cathodic protection but located between the ground anode and the structure, the ionic soil current may cause localised corrosion of unprotected buried structure as shown in fig.4.13 below.
- 4. If polarization is too weak, materials remain exposed to the corrosive medium and thus remaining unprotected.

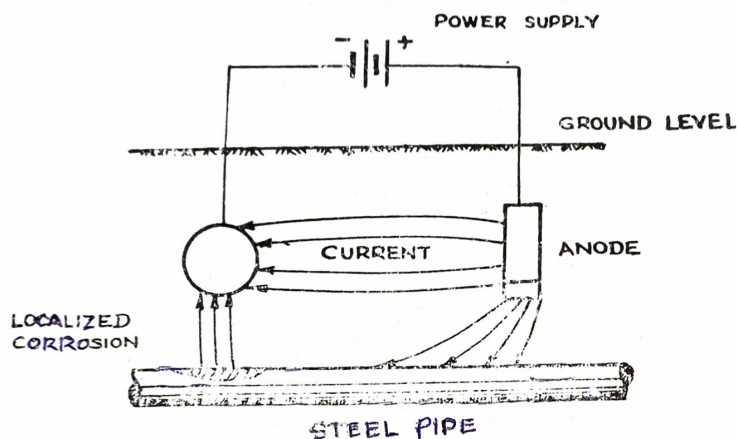


Fig.4.13 Localised corrosion of unprotected buried pipe.

4.3.2 Corrosion prevention by anodic protection

In contrast to cathodic protection, anodic protection is relatively new. It is based on the formation of a protective film on metals by externally applied anodic currents. It has been seen that by the application of anodic current to a structure, the rate of dissolution of metal increases and the rate of hydrogen evolution decreases. This only occurs except for metals with active - passive transitions such as nickel, iron, chromium, titanium and their alloys. If carefully controlled anodic currents are applied to those materials, they will become passivated and the rate of metal dissolution will decrease. The following figure shows an anodically protected steel storage tank containing sulphuric acid.

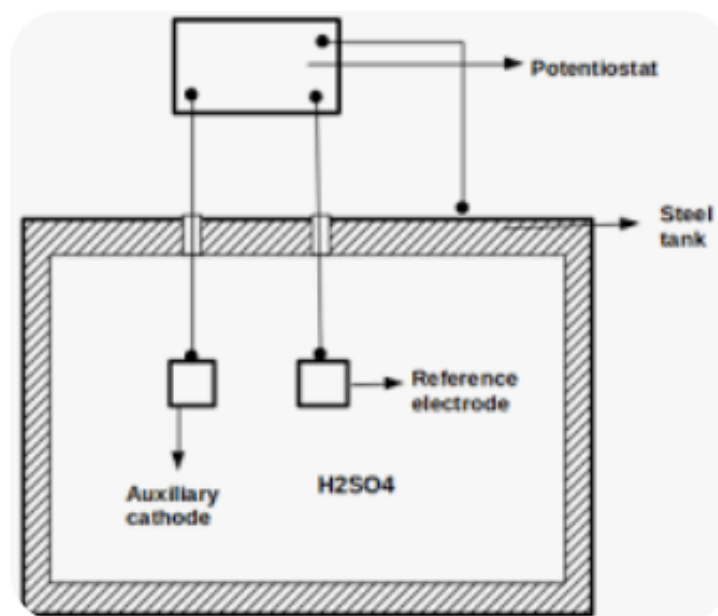


Fig.4.14 Scheme of anodically protected steel tank containing sulphuric acid.

To anodically protect a structure, a device called potentiostat is required, which maintains a metal at a constant potential with respect to a reference electrode. It has three terminals, one connected to the tank, another to an auxiliary cathode and third to a reference electrode.

In operation, the potentiostat maintains a constant potential between the tank and the reference electrode.

Requirements for anodic protection

The following requirements must be met for anodic protection:

1. The metals under consideration should exhibit passivity in the corrodent.
2. The protective film must be less than 100\AA thick.
3. The film must be an electronic conductor.
4. The film must be formed very rapidly, hydrophobic and oxidised.
5. The weight loss should be negligible in passive range.
6. Current to maintain passivity must be low.

Advantages of anodic protection method

The important advantages of anodic protection are described briefly below:

1. Improvement in product quality: Contamination of the product by the corrosion product of the container is much reduced by anodic protection.
2. Reduced capital investment.
3. Reduced maintenance cost.
4. Avoids stress corrosion cracking.
5. Reduced equipment cost.

Disadvantages of anodic protection method

Some of the limitations of this method are;

1. This method can not be applied in case of corrosive medium containing aggressive anions such as chloride.
2. If protection break down at any point, it is difficult to re-establish.
3. Anodic protection can not protect any metal immersed in any conducting media.

Applications of anodic protection

Anodic protection is used in the following systems:

1. Carbon steel equipment in contact with oleum, sulphuric acid, black sulphuric acid, super phosphoric acid, aqueous ammonia, aqueous ammonium nitrate, sodium carbonate, sodium hydroxide etc.
2. Stainless steel equipment in contact with sulphuric acid, oxalic acid, sodium carbonate, sodium hydroxide, aluminium sulphate solution, sulphonc acid, phosphoric acid, ammonium nitrate solution etc.
3. Chromium in contact with hydrofluoric acid.

Comparison between cathodic and anodic protection

<u>Cathodic protection.</u>	<u>Anodic protection</u>
1. It can be applied to all metals and weak to moderate corrosives.	1. It can be applied to metals which shows passive range and to weak to aggressive corrosives.
2. Lower installation cost	2. Higher installation cost.
3. Higher maintenance cost	3. Lower maintenance cost.
4. Operating conditions can be determined by empirical means	4. Operating conditions can be determined by electrochemical measurements.

4.3.3 Passivity

It is known that certain metals and alloys can exist in two states - active and passive. In active state, metal exhibits greater activity with respect to certain type of environments than others. While in passive state, metals and alloys behave as if these are more noble i.e, have a lower position in the e.m.f. series. For example, iron in dilute nitric acid is active while in concentrated nitric acid, it is passive. Thus in the former case, dilute nitric acid can not be stored in iron vessel while in latter case, it can be stored.

The phenomenon of passive state is known as passivity. Thus passivity may be defined in the following two ways:

Thermodynamically, "passivity is the phenomena by which metal remains unattacked in a medium in which a net decrease of free energy is associated with the corrosion reactions".

Electrochemically, "passivity is the phenomena by which metal, when acting an anode in electrolysis does not pass into solution even though the value of equilibrium potential seems to indicate that it should.

